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THE DEVELOPMENT OF HIGH TEMPERATURE STABLE POLYIMIDE STRUCTURAL ADHESIVES

E. A. ARVAY
T. J. APONYI

TECHNICAL REPORT AFML-TR-71-3

APRIL 1971

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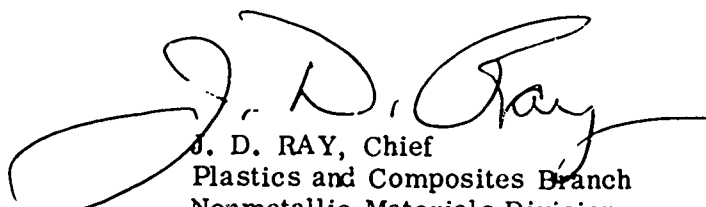
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FOREWORD

This report was prepared by E. A. Arvey and T. J. Aponyi, of the Plastics and Composites Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. The in-house work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734002, "Structural Adhesives." The work was administered under the direction of the Air Force Materials Laboratory. The research reported in this document constitutes a portion of studies conducted from the period 1 July 1968 to 30 June 1969. This report was submitted by the authors in December 1969 for publication as a technical report.

The authors gratefully acknowledge the contributions made by Messrs. P. W. Centers, W. E. Click, and R. J. Kuhbander in the formulation of adhesives, preparation of adhesive bonded joints, and testing.

This technical report has been reviewed and is approved.



J. D. RAY, Chief
Plastics and Composites Branch
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Air Force Materials Laboratory

ABSTRACT

A new polyimide resin, AF-R-2009, which had exhibited an oxidative stability superior to that of commercially available polyimides under isothermal aging at 700°F was formulated into a series of adhesives. The respective adhesives were used to bond Ti-8Al-1V-1Mo titanium and 17-7 PH stainless steel alloy adherends. Tensile lap shear strength properties were determined at room temperature and at 600 and 700°F after isothermal aging at the respective temperatures. One formulation of the AF-A-2009 adhesive was essentially equivalent to commercially available polyimide adhesives at 600°F exposure with both titanium and stainless steel adherends. The effects of varying the concentration of antioxidant, arsenic thioarsenate, on bonded joint strengths were determined. The need for improved surface treatments for titanium adherends was substantiated by the bonded joint strength data obtained with the experimental adhesive. The infrared (IR) spectra of the respective formulations were obtained to study the B-staging and cure processes and to determine the effect of additives on the respective IR spectra.

TABLE OF CONTENTS

SECTION	PAGE
I INTRODUCTION	1
II TECHNICAL DISCUSSION	2
1. AF-R-2009 Polymer Chemistry	2
2. AF-R-2009 Composite Properties	5
III EXPERIMENTAL	8
1. Procedures	8
a. Formulation	8
(1) Aluminum	9
(2) Antioxidant	10
b. Bonding	10
(1) Tape Preparation	10
(2) Surface Preparation	13
(a) 17-7 PH Stainless Steel	13
(b) 8-1-1 Titanium	13
(3) Primer Application	14
(4) Bonding	14
c. Testing	16
2. Results and Discussion	16
a. Tensile Lap Shear Strengths	16
(1) Stainless Steel at Room Temperature	20
(2) Stainless Steel Aging at 600°F	20
(3) Stainless Steel Aging at 700°F	25
(4) Titanium Tests at Room Temperature	33
(5) Titanium at 600°F	38
(6) Titanium at 700°F	45

TABLE OF CONTENTS (Contd)

SECTION	PAGE
b. Comparison of AF-A-2009 Adhesives To A Commercially Available Polyimide Adhesive	54
c. Infrared Spectra Study Results	62
(1) Formulation D	64
(2) Formulation E	66
(3) Formulation C	69
(4) Formulation A	71
(5) Formulation B	74
(6) Summary	76
IV SUMMARY	77
BIBLIOGRAPHY	78

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1.	Formation of Amic Acid Prepolymer	3
2.	Sequence of Reactions Leading to Formulation of AF-R-2009 Polymer	4
3.	Flexural Strength Versus Heat Aging at 600°F on AF-R-2009 and Commercial Polyimide Glass Cloth Reinforced Composites	7
4.	Blending of Ingredients to Prepare an AF-A-2009 Adhesive Formulation	11
5.	Impregnating Apparatus for Preparing Adhesive Tapes	12
6.	Adhesive-Bonded Finger Panel and Individual Test Specimen	15
7.	Separation of Bonded Lap Shear Specimens from Bonded Panel Using a Cutoff Wheel	17
8.	Positioning Specimen in Test Fixture in Hot Test Oven	18
9.	Tensile Lap-Shear Specimen in Loading Fixture Prior to Testing	19
10.	Effect of 600°F Heat Aging on Tensile Lap-Shear Strength of AF-A-2009 and FM-34 Adhesive-Bonded Titanium Joints	55
11.	Effect of 600°F Heat Aging on Tensile Lap-Shear Strength of AF-A-2009 and FM-34 Adhesive-Bonded Stainless Steel Joints	56
12.	Effect of 700°F Heat Aging on Tensile Lap-Shear Strength of AF-A-2009 and FM-34 Adhesive-Bonded Titanium Joints	57
13.	Effect of 700°F Heat Aging on Tensile Lap-Shear Strength of AF-A-2009 and FM-34 Adhesive-Bonded Stainless Steel Joints	58
14.	IR Spectra of AF-A-2009, Formulation D, on a KBr Salt Window	65
15.	IR Spectra of AF-A-2009, Formulation E, on a KBr Salt Window	68
16.	IR Spectra of AF-A-2009, Formulation C, on a KBr Salt Window	70

LIST OF ILLUSTRATIONS (Contd)

FIGURE		PAGE
17.	IR Spectra of AF-A-2009, Formulation A, on a KBr Salt Window	72
18.	IR Spectra of AF-A-2009, Formulation B, on a KBr Salt Window	75

LIST OF TABLES

TABLE		PAGE
I	Flexural Properties Vs. Heat Aging at 700°F In Air of AF-R-2009 and Commercial Polyimide Composites	6
II	AF-R-2009 Polyimide Adhesive Formulations	9
III	Tensile Shear Strengths of AF-A-2009 Formulations at Room Temperature	21
IV	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 1/2 Hr at 600°F	22
V	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 50 Hr at 600°F	23
VI	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 100 Hr at 600°F	24
VII	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 200 Hr at 600°F	26
VIII	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 500 Hrs at 600°F	27
IX	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 750 Hrs at 600°F	28
X	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 1000 Hrs at 600°F	29
XI	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 1200 Hrs at 600°F	30
XII	Tensile Shear Strengths of AF-A-2009 Formulations at 700°F After 1/2 Hrs at 700°F	31
XIII	Tensile Shear Strengths of AF-A-2009 Formulations at 700°F After 24 Hrs at 700°F	32
XIV	Tensile Shear Strengths of AF-A-2009 Formulations at 700°F After 50 Hrs at 700°F	34
XV	Tensile Shear Strengths of AF-A-2009 Formulations at 700°F After 75 Hrs at 700°F	35
XVI	Tensile Shear Strengths of AF-A-2009 Formulations at 700°F After 100 Hrs at 700°F	36

LIST OF TABLES (Contd)

TABLE		PAGE
XVII	Tensile Shear Strengths of AF-A-2009 Formulations at Room Temperature	37
XVIII	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 1/2 Hr at 600°F	39
XIX	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 50 Hrs at 600°F	40
XX	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 100 Hrs at 600°F	41
XXI	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 200 Hrs at 600°F	42
XXII	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 500 Hrs at 600°F	43
XXIII	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 750 Hrs at 600°F	44
XXIV	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 1000 Hrs at 600°F	46
XXV	Tensile Shear Strengths of AF-A-2009 Formulations at 600°F After 1200 Hrs at 600°F	47
XXVI	Tensile Shear Strengths of AF-A-2009 Formulations at 700°F After 1/2 Hr at 700°F	48
XXVII	Tensile Shear Strengths of AF-A-2009 Formulations at 700°F After 24 Hrs at 700°F	50
XXVIII	Tensile Shear Strengths of AF-A-2009 Formulations at 700°F After 50 Hrs at 700°F	51
XXIX	Tensile Shear Strengths of AF-A-2009 Formulations at 700°F After 75 Hrs at 700°F	52
XXX	Tensile Shear Strengths of AF-A-2009 Formulations at 700°F After 100 Hrs at 700°F	53
XXXI	Infrared Adsorption Peaks	63

SECTION I

INTRODUCTION

The continuous demand for increasing performance characteristics of Air Force aircraft necessitates the development of adhesives which can improve the strength properties, useful life at elevated temperature, reliability, and durability of adhesive bonded primary and secondary structural components on such aircraft. Consequently, any polymer which exhibits resistance to oxidative degradation at temperatures of 600°F and above is a logical candidate for formulation into adhesives and subsequent characterization of bonded joint strength properties at room temperature and at elevated temperatures under isothermal aging conditions.

Under a contract with the Nonmetallic Materials Division, the Monsanto Research Corporation synthesized a novel polyimide polymer, designated AF-R-2009, which exhibited an oxidative stability superior to that of the best commercially available polyimide when used as a matrix in glass cloth reinforced composites. In addition, composites with the AF-R-2009 polymer as matrix could be press cured at 500°F compared to the 600°F press cure required for the commercial polyimides.

The purpose of the effort described in this report was to develop a high temperature structural adhesive from the AF-R-2009 resin. The effort included not only the formulation of adhesives by the addition of a metallic filler and arsenic thioarsenate as an antioxidant but also a definition of the effects on oxidative stability of the adhesive by variations in the ratio of antioxidant used in adhesive formulation and the determination of the strength versus time at elevated temperature profile of joints bonded with the unfilled resin, i. e., no filler or antioxidant added. Adherends used to prepare test specimens were 17-7 PH stainless steel alloy (annealed) and Ti-8Al-1V-1 Mo titanium alloy (duplex annealed).

SECTION II

TECHNICAL DISCUSSION

1. AF-R-2009 POLYMER CHEMISTRY

High temperature polyimide resins are the products of the condensation reaction between aromatic tetra acids or tetracarboxylic dianhydrides and aromatic diamines. Typical acid moieties include pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) while the most common diamines include m-phenylene diamine (mPDA), oxydianiline (ODA), and methylene dianiline (MDA). The most common commercially available resins are synthesized from BTDA and mPDA, or ODA.

The polymer is a prime candidate for use in high temperature applications, since it has exhibited the highest level of oxidative stability under isothermal aging at 600 and 700°F. In addition, the B-staged prepolymer is soluble and has good flow and fusion characteristics which are prerequisites for the preparation of high strength reinforced plastic composites and adhesive-bonded joints.

Polyimide prepolymers are prepared by reacting the dianhydride and diamine monomers in suitable solvents, such as dimethylacetamide (DMAC), dimethylformamide (DMF), or N-methyl pyrrolidone (NMP). Reaction temperature varies between 40 and 60°C, during which the anhydride ring opens and one amino hydrogen atom transfers to a carboxyl group, and the other carboxyl group then reacts with the amino group to form an amic acid prepolymer as shown in Figure 1.

The prepolymer is soluble in the solvent used during the reaction. Solute concentrations range from 50 to 65% by weight. As a solution the prepolymer may be readily used to impregnate reinforcements such as glass cloth and roving, boron filaments, and graphite yarn. The impregnated reinforcement may then be dried and the resin advanced (B-staged) to predetermined levels consistent with flow and fusion properties required to obtain a dense composite or adhesive glue-line.

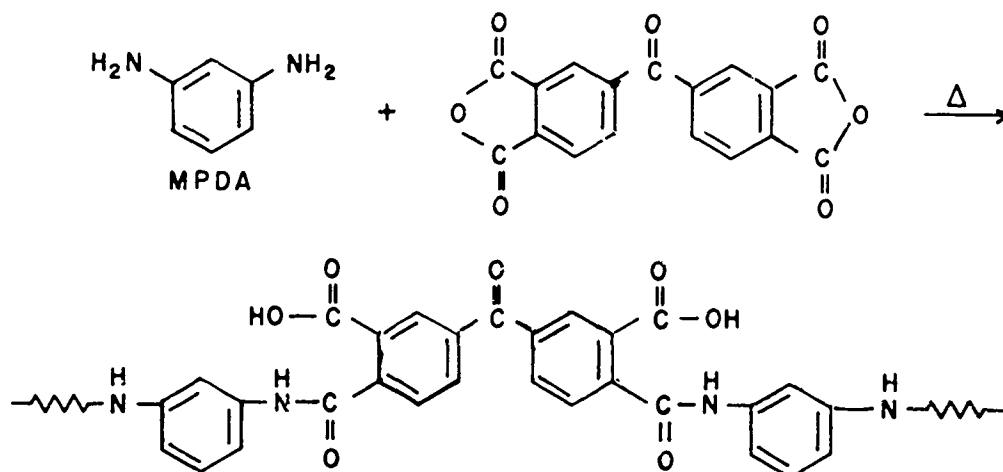


Figure 1. Formation of Amic Acid Prepolymer

The polyimide prepolymer is cured by the application of heat. During cure the amide hydrogen combines with the acid OH to form water (which is driven off as a vapor) and the imide ring. Press cure of reinforced composites requires a temperature of 600°F while the autoclave cure can be accomplished at 350°F. Structures, either composites or adhesive-bonded joints, cured by the autoclave technique must be postcured under a programmed schedule to a temperature at least equal to the service temperature to which the structure will be exposed.

The AF-R-2009 polyimide has the same molecular structure as most commercial polyimides when fully cured. However, a structural dissimilarity exists in the prepolymer stage. In the B-stage condition AF-R-2009 has an amide-ester structure as illustrated in Figure 2.

The volatile compound evolved during the imide ring closure, ethylene glycol, is also the solvent for the AF-R-2009 prepolymer. This fact is considered to be beneficial to the cure of the polymer because the glycol can act as a plasticizer for the resin during ring closure. It is postulated that plasticization of the polymer during cure results in a more complete cure, since the resin retains sufficient fluidity to enable additional end groups to

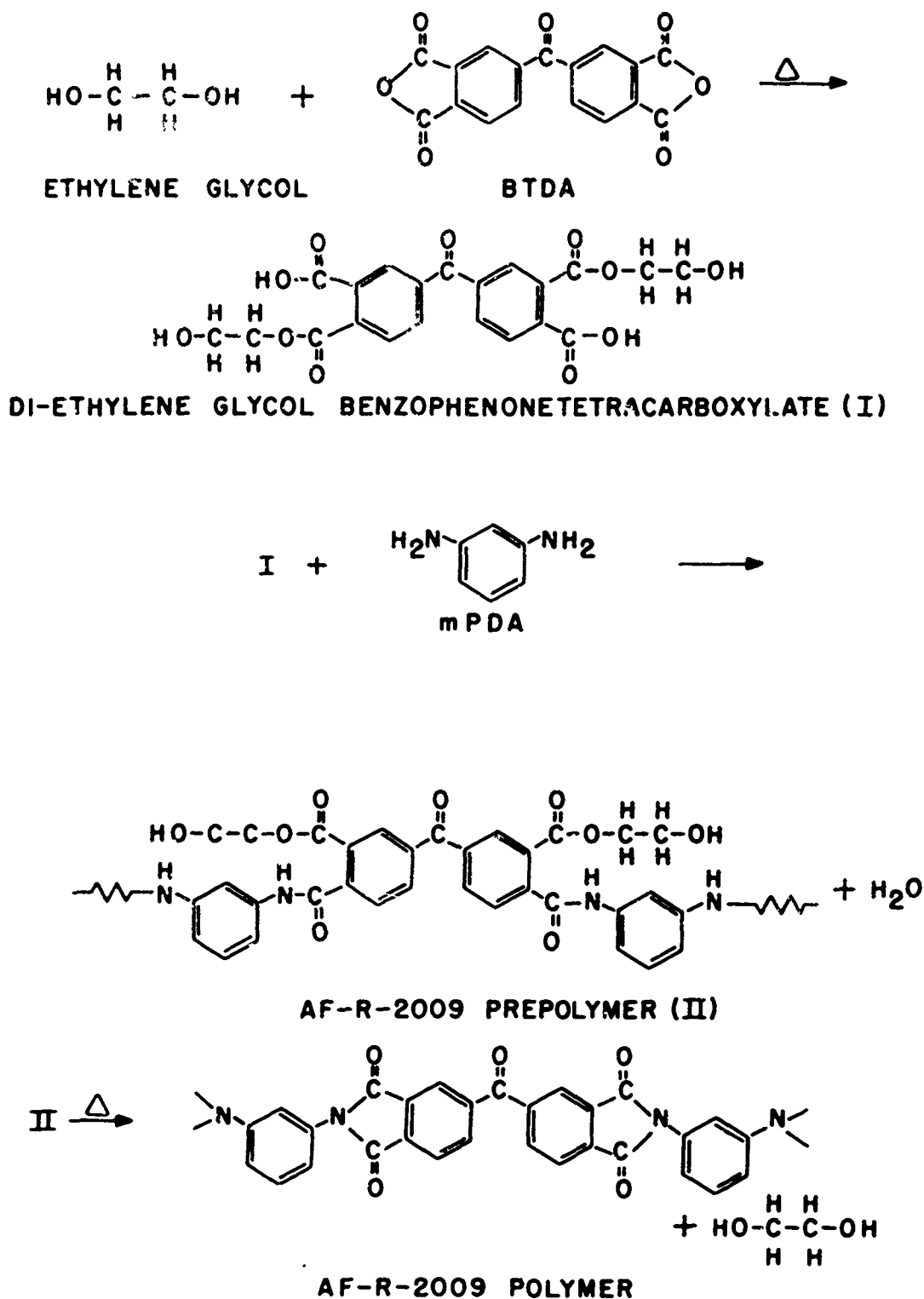


Figure 2. Sequence of Reactions Leading to Formulation of AF-R-2009 Polymer

react, thereby increasing the molecular weight of the cured resin and enabling the matrix to be compacted into a denser mass. Under nonplasticized cure conditions, e.g., evolution of water during cure, the resin reaches a comparatively intractable, infusible state at a lower degree of polymerization.

Either of the two effects of plasticization should be reflected by an increase in oxidative stability of reinforced composites subjected to isothermal aging at elevated temperatures. In addition, the plasticizer was expected to provide an equivalent degree of cure of the AF-R-2009 resin at temperatures below those required for state-of-the-art polyimides (600°F) when the press cure cycle was employed. All the anticipated improvements were realized during the fabrication of glass cloth reinforced composites and subsequent characterization of flexural strength properties of test specimens heat aged isothermally at 700°F.

2. AF-R-2009 COMPOSITE PROPERTIES

Glass cloth reinforced composites were fabricated with the AF-R-2009 resin as matrix for the purpose of determining the flexural properties of the composites as a function of isothermal heat aging at 600 and 700°F. A study was also made to determine the lowest press-cure temperature which would result in reproducible high strength, high quality composites. The reinforcement used for 700°F exposure specimens was style 181 S glass cloth, heat cleaned. Heat-cleaned glass was used to minimize any loss of mechanical properties because of decomposition of an organo-silane finish or size with a resultant loss of matrix/reinforcement interfacial bond. Laminates prepared for 600°F exposure were made with Style 181 E glass cloth with A-1100 soft finish.

The AF-R-2009 was found to be more amenable to lower temperature press curing than its commercially available counterparts. High quality composites were prepared with a cure cycle of one hour at 500°F under 200 psi pressure, compared to the usual one hour at 600°F and 200 psi pressure required for commercial polyimides. The postcure used to advance the matrix resins to a higher degree of polymerization was two hours each at 392, 437, 482, 572, 617, and 662°F, then four hours at 700°F in air.

Figure 3 shows a plot of flexural strength versus heat aging at 600°F in air of AF-R-2009 and commercial polyimide composites. Generally, the AF-R-2009 composite exhibited 10 to 20% lower flexural properties than the commercial version. However, at 700° this trend was reversed, as shown in Table I.

TABLE I
FLEXURAL PROPERTIES VS. HEAT AGING AT 700°F IN AIR OF
AF-R-2009 AND COMMERCIAL POLYIMIDE COMPOSITES

Reinforcement: Style 181 S Glass, Heat Cleaned				
Exposure	AF-R-2009		Commercial	
	Strength psi x 10 ³	Modulus psi x 10 ⁶	Strength psi x 10 ³	Modulus psi x 10 ⁶
R. T.	55.3	3.3	54.5	2.9
1/2 hr @ 700°F	21.5	1.0	19.7	0.8
100 hr @ 700°F	40.5	2.9	34.4	2.7

The reason for anomalous behavior of the AF-R-2009 is not known. The unexpectedly low room temperature flexural strength may be a contributing factor to the inferior performance at 600°F. The cure cycle was not optimized and this fact may account for the low room temperature values. However, the isothermal behavior at 700°F is indicative of the improved oxidative stability of the AF-R-2009 polymer.

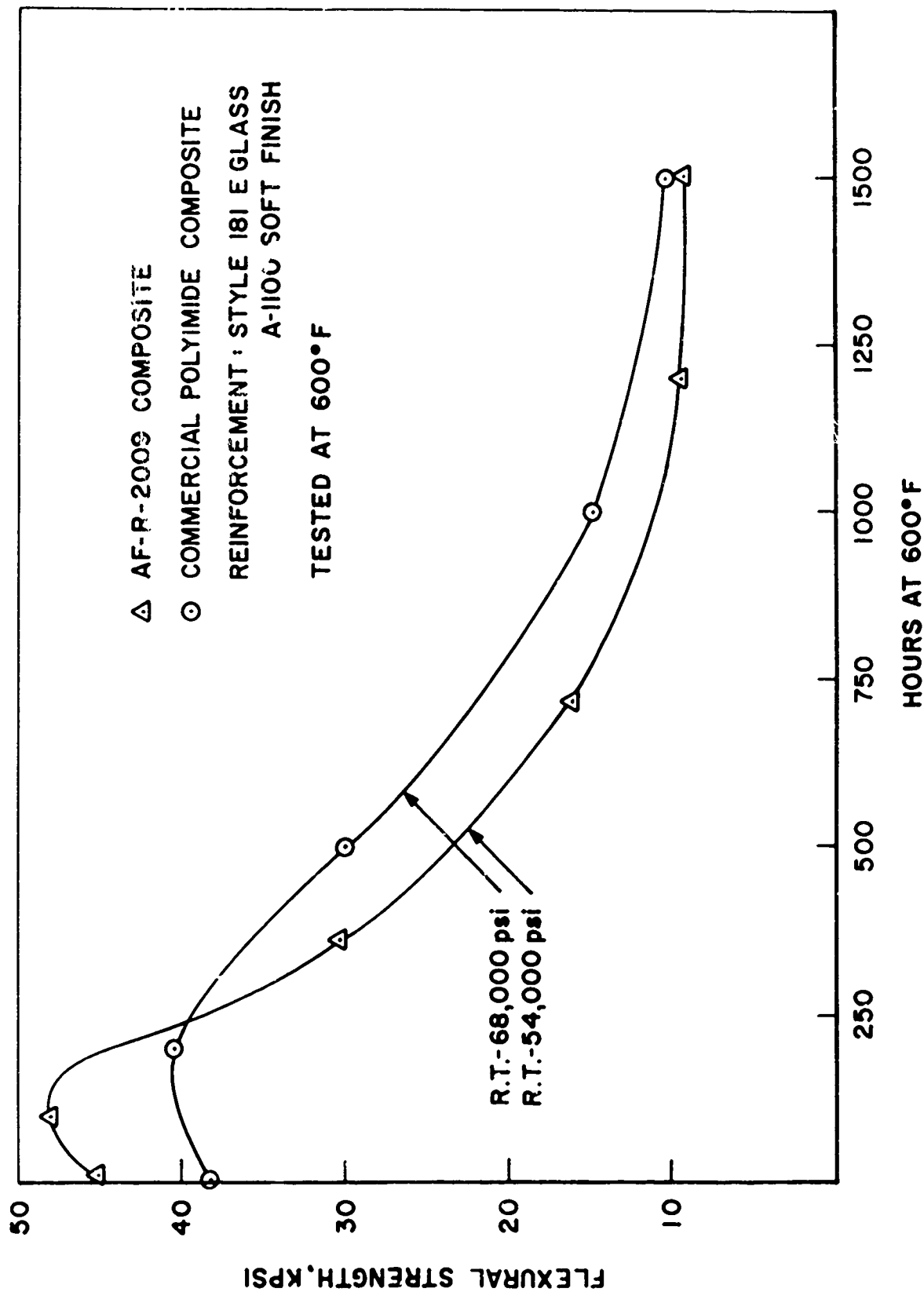


Figure 3. Flexural Strength Versus Heat Aging at 600°F on AF-R-2009 and Commercial Polyimide Glass Cloth Reinforced Composites

SECTION III

EXPERIMENTAL

1. PROCEDURES

The procedures described in detail in the following paragraphs are standard for the evaluation of candidate polymers as adhesives. The nature and behavior of a polymer will dictate modifications from time to time as will the introduction of a second variable such as a new surface preparation, new adherend, or a new curing technique. Procedures utilized herein represent an initial evaluation rather than an optimization.

a. Formulation

Generally, the cohesive strength (in the shear mode) of a "clear" or "neat" resin when utilized as an adhesive is not sufficiently high at either room temperature or at elevated temperature. The polymerization of a resin between the adherends does not allow for either good wetting contact, modifies the resin properties, undergoes a stress riser process, or a combination of all of these. At elevated temperatures a neat resin suffers from differential thermal expansion as compared to the adherends, suffers degradation, or undergoes accelerated degradation due to the presence of and contact with the adherend.

To eliminate as many of these deleterious conditions as possible, additives are introduced into the resin. Additives commonly used include solvents or diluents to decrease the viscosity (increasing wetting contact), metallic fillers to reduce the differences in the thermal expansion coefficients, surfactants to increase wetting, inert nonmetallic fillers to increase viscosity (to reduce properties, thixotroper), and an antioxidant to deter oxidative degradation. Other additives may be used to increase the efficiency of the adhesive or to decrease the cure time or temperature, for example. Many adhesives contain one or more other polymers to effect changes in rheology or other adhesive property.

In this program, representing an initial evaluation of a polymeric adhesive base, only two additives were utilized. Aluminum powder was added for expansion control and arsenic thioarsenate as an antioxidant. This combination has, in the past, provided a sufficient modification of the polymer properties for a reliable evaluation.

The AF-R-2009 polyimide resin was formulated with varying proportions of the two additives. Table II lists the proportions used in the experimental formulations.

TABLE II
AF-R-2009 POLYIMIDE ADHESIVE FORMULATIONS

Formulation Designation	Alternate Designation	Resin	Aluminum phr	AsAsS ₄ phr
A	20:1	100	100	20
B	10:1	100	100	10
C	25:1	100	100	25
D	0:0	100	0	0
E	0:1	100	100	0

The alternate formulation designation provides a rapid index of the composition as parts per hundred of resin (phr) and the ratio of aluminum to resin. A typical adhesive formulation size was based upon 200 grams of AF-R-2009, polyimide resin.

(1) Aluminum

Aluminum powder, after weighing to approximately 0.01 gm on a top loading, direct reading balance was added to the resin. Intimate wetting of the dry powder by the resin was aided by the use of a mixer with a straight stainless steel rotor turning at approximately 30 rpm. The resin-powder mixture was blended by a shearing action between the rotor and the side of a beaker. This technique is adequate for the small adhesive batches formulated during this

program. The aluminum powder used was finely divided with an analysis rating of 100 mesh. Figure 4 shows the mixing of a formulation.

(2) Antioxidant

The antioxidant used in these formulations is arsenic thioarsenate (AsAsS_4). Prior to adding to the resin-aluminum mixture, the antioxidant was hand pulverized using mortar and pestle. The resultant fine powder was then weighed to within 0.01 grams of the specified amount. Blending was again accomplished using the shearing action provided by the stainless steel rotating shaft and the glass beaker. The combination of prepulverizing and shearing results in a smooth, well mixed adhesive paste.

b. Bonding

The bonding procedures for any adhesive adherend system are in many cases the result of a long series of systematic variations of process parameters. Thus, the preparation of the adhesive tape and the subsequent B-staging of the tape are based upon observations and experience with this type of resin. The preparation of the adherend is based upon standard preparations used exclusively in evaluating materials as adhesives. Cure and postcure cycles are based upon data accumulated with the resin in structural, reinforced composites. Each of these will be described in detail in the following sections.

(1) Tape Preparation

The relatively small quantities of polymers generally available for evaluation has led to the fabrication of a simple impregnation process. Although the process appears to be unsophisticated as compared to some commercial facilities, excellent results in wetting and thickness control have been obtained. The tape making apparatus, a simple double roller, doctor blade, and pan arrangement, is shown in Figure 5.

The carrier fabric, style 112, heat cleaned E-glass fabric, used throughout this and other evaluations provides the handling characteristics and glue-line-thickness "control" desired. The adhesive formulations, or portions thereof, were placed in the resin pan and heated at 120°F in a circulating water bath. The carrier fabric, cut into strips approximately 2-3/4 inches by 36 inches,



Figure 4. Blending of Ingredients to Prepare an AF-A-2009 Adhesive Formulation

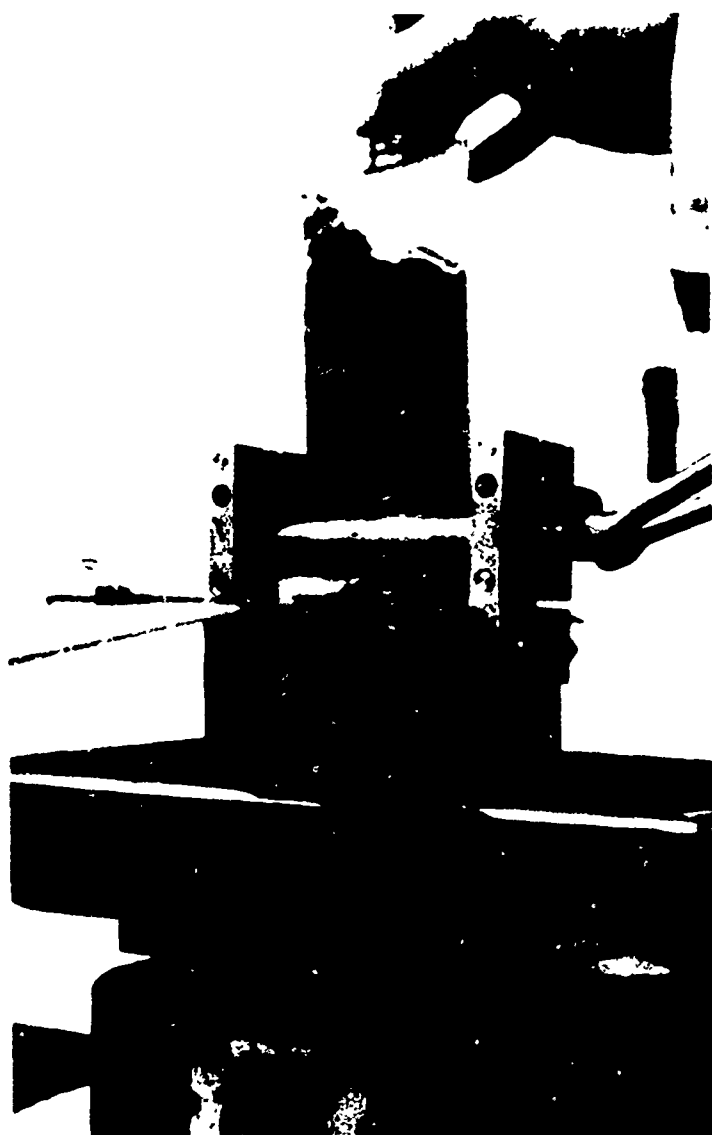


Figure 5. Impregnating Apparatus for Preparing Adhesive Tapes

was pulled through the formulation and through the opposed rollers which were spaced at approximately 0.014 inch. The rollers of stainless steel provide some mechanical forcing of the adhesive into the carrier, which removes excess adhesive. The glass fabric can be pulled mechanically by a motor pulley, by cable arrangement, or manually. The impregnated fabric was then cut into shorter lengths and mounted vertically by mechanical devices in a circulating air oven set at 212°F. The adhesive tapes were staged for 45 minutes at this temperature. Staging has several effects and purposes: It 1) allows for greater wetting, 2) reduces the solvent content, and 3) renders the tape less tacky. The staging conditions have been found not to advance the resin polymerization but only to reduce the volatile content. The prepared tapes were then removed and stored in sealed polyethylene bags at approximately 40°F. The tapes were removed, as needed, just prior to use.

(2) Surface Preparation

The two adherends, 17-7 PH stainless steel and 8 Al-1 Mo-1V titanium alloy, were treated with the same solution with only the temperature varying. The complete procedures are given below:

(a) 17-7 PH Stainless Steel - This adherend as prepunched, preslotted 4 inch x 9 inch panels is used exclusively. The 4 x 9 panels provide seven individual test specimens after bonding and completing the slots. Approximately 1 inch of each panel was prepared for bonding by the following steps:

- Step 1 Wash panel in an Alconox solution and rinse.
- Step 2 Degrease in condensing trichloroethylene vapor 10 minutes.
- Step 3 Immerse dry panel for 4 minutes in a 160 to 170°F acid bath consisting of:

Orthophosphoric acid (85%)	841 ml
Hydrochloric Acid (38%)	87 ml
Hydrofluoric acid (48%)	56 ml
- Step 4 Rinse panel with water and check for "water break."
- Step 5 Force-dry panel with hot air gun.

(b) 8-1-1 Titanium - Each preslotted and prepunched 4 inch x 9 inch panel was prepared by

- Step 1 Degreasing in condensing trichloroethylene vapors 10 minutes.

Step 2 Immersing, dry, for 2 minutes in an RT acid bath consisting of the same composition as in Step 3 above.

Step 3 Rinsing with water

Step 4 Force-drying with hot air.

(3) Primer Application

Both adherends, stainless steel and titanium, were primed using a small portion of the adhesive formulation. The primer was applied with a spatula to a thickness of 1 to 2 mils. The primed panels were then oven dried for 45 minutes at 212°F.

(4) Bonding

The primed panels were assembled in a bonding jig by placing a 5/8 inch wide strip of adhesive tape between the primed panels. The panels were positioned and secured to provide a nominal 1/2 inch overlap. Shims were used to ensure parallellism of the panels. Aluminum foil was used as a separating film to prevent bonding of the panels to the bonding jig. A pressure bar was placed over the overlap of the two panels to transmit pressure to the faying surfaces of the panels.

The bonding jig with the assembled panels was placed into a heated platen press (Wabash Metal Products). The glue-line temperature was monitored by a thermocouple placed next to the joint area. The platens were preheated to 600°F, the jig inserted, and the press closed to contact pressure. When the glue-line temperature reached 600°F, 25 psi pressure was applied across the overlap joint area. The time at temperature was begun when the glue-line temperature reached 600°F as recorded on a separate recorder (Brown). The cure cycle was one hour at 600°F and 25 psi. At the end of the cycle the press platens were water cooled to 300°F or less prior to removal of the bonding jig. After further cooling to handling temperature the panels were removed from the jig. No postcure was used on these panels. Each specimen was identified with a number code. See Figure 6 for completed panel.

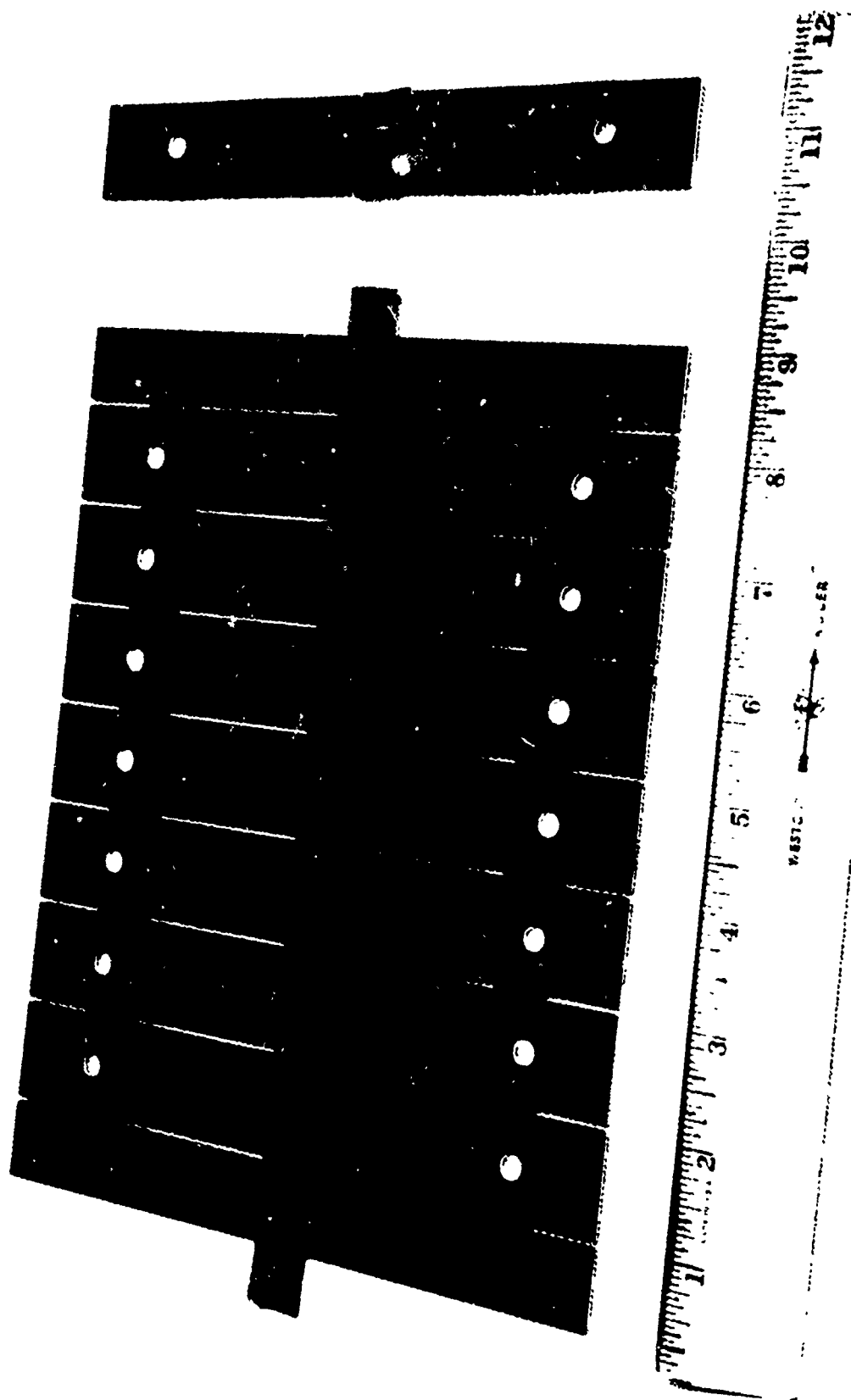


Figure 6. Adhesive-Bonded Finger Panel and Individual Test Specimen

c. Testing

The 1/2 inch overlap, tensile shear panels were separated into individual specimens using a cutoff wheel with minimal water spray as a coolant. See Figure 7. Individual specimens were measured for thickness, width, and bond length to the nearest 0.001 inch and recorded. Test specimens were randomly selected for testing at the various temperatures. Aging of the specimens was done in circulating air ovens at the specified temperature $\pm 5^{\circ}\text{F}$. Long-time aging specimens were aged to within one hour of the specified time and then completed in the test oven. Short-time, i.e., 1/2 and 1 hour aging specimens, were aged in the test oven.

All specimens were tested in accordance with the Federal Test Standard 175 and Military Specification MMM-A-132 except for the use of higher temperatures of 600 and 700 $^{\circ}\text{F}$. The rate of loading was 1200 lb/sq in/min for the 1/2 square inch tensile lap shear specimens. Procedures and test fixtures are shown in Figures 8 and 9. All breaking loads were recorded and ultimate lap shear strengths calculated.

2. RESULTS AND DISCUSSION

a. Tensile Lap Shear Strengths

Bonded specimens were prepared with each of the formulations and aged for various periods of 600 and 700 $^{\circ}\text{F}$. The aging periods at 600 $^{\circ}\text{F}$ ranged from 1/2 hour to 1200 hours. At 700 $^{\circ}\text{F}$ the periods ranged from 1/2 hour to 100 hours. After aging, the specimens were tested at the same temperature at which they were aged. Room temperature strength data was obtained on each formulation on each of the two metallic adherends.

Test data are presented below on five experimental adhesives, one cure cycle, and one treatment for each adherend. It is emphasized that no optimization of the cure cycle was attempted and that no modification of the adherend preparation was made. The data compares the five formulations on each adherend at the test temperatures.



Figure 7. Separation of Bonded Lap Shear Specimens from Bonded Panel Using a Cutoff Wheel



Figure 8. Positioning Specimen in Test Fixture in Hot Test Oven

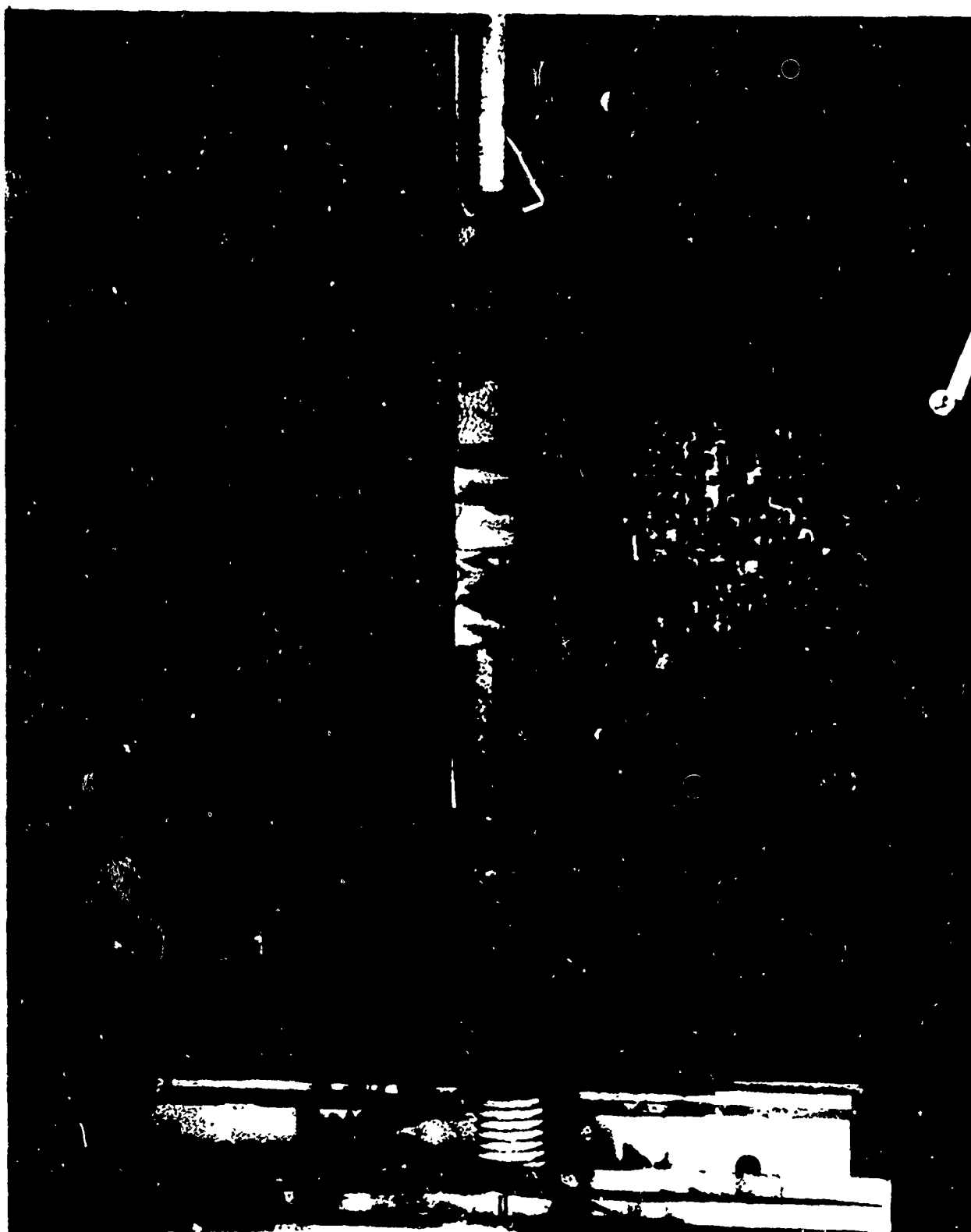


Figure 9. Tensile Lap-Shear Specimen in Loading Fixture Prior to Testing

(1) Stainless Steel at Room Temperature

Table III gives the room temperature (R. T.) results on stainless steel adherends. The results are based upon three specimens, one from each of three different panels bonded with the same formulation. The neat resin (0, 0) produced a joint strength averaging 2827 psi. The addition of aluminum powder (0, 1) increased the strength to 3276 psi. The three formulations with antioxidant added gave 2997 (10, 11), 2867 (20, 1), and 2933 (25, 1). This additive with aluminum resulted in lower strengths than with aluminum alone, but higher than the neat resin. The range of the values between specimens, 100 to 330 psi, is not excessive and indicates reliable results.

(2) Stainless Steel Aging at 600°F

The data for the 1/2 hour aging at temperature shown on Table IV, generally shows the same increase, decrease trend seen in the R. T. data. The neat resin produces the lowest strength, the resin/aluminum the highest, the antioxidant formulations somewhat less than the 0, 1 formulation. The order of the antioxidant formulations' strengths, however, is not consistent. At room temperature the order was 10>25>20, after 1/2 hour aging a 20>25>10 pattern was set. The spread between these three at temperature is only 82 psi. The large decrease in strengths, 40 to 48% after 1/2 hour temperature, is evidently a property of the polyimide resin. Such reductions are seen also in polyimide composites. There is no good explanation for this remarkable drop in strength.

After 50 hours' aging, the results in Table V show a great leveling effect. The 0, 1 formulation leads at 2144 psi, closely followed by the other four, 10, 1 (2093 psi), 25, 1 (2043), 0, 0 (2022 psi), and 20, 1 (1967 psi). At this point only a 116 psi spread covers the last four. Note that the strengths have recovered from the previous point (1/2 hour) minima. After 50 hours' aging there is no good basis for selecting one formulation over another.

The 100 hours' aging data begins to show the benefit of the antioxidant additive. Table VI shows the 10 and 20 phr antioxidant formulation as essentially equal, the 0, 1 formulation at 1981 psi, and the 25, 1 formulation at 1950 psi. The neat resin appears to be failing.

TABLE III

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT ROOM TEMPERATURE

Adherend: 17-7 PH Stainless Steel, Annealed						
Surface Treatment: Standard Phosphate Etch						
Formulation	Maxium Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	1320	2780			.004	
	1390	2810			.005	
	1400	<u>2890</u>			.004	
Av.		2827	110	46		100
E	1550	3195			.010	
	1614	3396			.009	
	1571	<u>3239</u>			.008	
Av.		3276	201	86		100
B	1470	2940			.009	
	1520	3170			.007	
	1440	<u>2880</u>			.009	
Av.		2997	290	125		100
A	1400	2800			.011	
	1450	2900			.009	
	1420	<u>2900</u>			.012	
Av.		2867	100	47		100
C	1360	2830			.007	
	1450	3050			.007	
	1390	<u>2920</u>			.009	
Av.		2933	220	90		100

TABLE IV

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 1/2 HR @ 600°F

Adherend: 17-7 PH Stainless Steel, Annealed						
Surface Treatment: Standard Phosphate Etch						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	676	1380			.003	
	814	1661			.003	
	704	1422			.003	
Av.		1488	281	124		53
E	801	1704			.009	
	791	1683			.008	
	884	1860			.008	
Av.		1749	173	79		54
B	706	1471			.009	
	827	1790			.009	
	783	1598			.009	
Av.		1620	319	131		54
A	772	1591			.009	
	840	1714			.010	
	882	1800			.009	
Av.		1702	209	86		60
C	753	1590			.011	
	793	1687			.011	
	798	1679			.011	
Av.		1652	97	44		52

TABLE V

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 50 HRS @ 600°F

Adherend: 17-7 PH Stainless Steel, Annealed						
Surface Treatment: Standard Phosphate Etch						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	1010	2020			.004	
	1002	2045			.003	
	981	2000			.004	
Av.		2022	45	18		72
E	1027	2161			.009	
	1027	2096			.010	
	1044	2175			.009	
Av.		2144	79	34		66
B	1059	2160			.007	
	1046	2090			.007	
	974	2030			.008	
Av.		2093	130	53		70
A	911	1860			.012	
	984	2010			.008	
	993	2030			.012	
Av.		1967	170	76		69
C	1010	2100			.010	
	904	1900			.008	
	1002	2130			.009	
Av.		2043	230	102		70

TABLE VI

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 100 HRS @ 600°F

Adherend: 17-7 PH Stainless Steel, Annealed						
Surface Treatment: Standard Phosphate Etch						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	769	1569			.003	
	1032	2106			.004	
	835	<u>1670</u>			.003	
Av.		1782	537	233		63
E	908	1892			.010	
	940	1958			.009	
	1047	<u>2094</u>			.009	
Av.		1981	202	84		61
B	1005	2051			.008	
	1050	2100			.007	
	1098	<u>2241</u>			.009	
Av.		2131	190	81		71
A	1002	2045			.011	
	1085	2170			.008	
	1075	<u>2194</u>			.010	
Av.		2136	149	65		74
C	1047	2013			.009	
	947	1933			.011	
	933	<u>1904</u>			.010	
Av.		1950	109	46		67

The 200 hours' aging data given in Table VII clearly indicates the failure of the neat resin and the resin-aluminum formulation as well. The three antioxidant formulations are very close at 2149, 2165, and 2074 psi for the 10, 20, and 25 phr formulations, respectively.

Table VIII lists the data for the 500 hours' aging of the formulations. Here the two non-antioxidant types are degraded almost completely. The resin-aluminum failed to survive the aging, and the neat resin retains a 120 psi joint strength. The 10 and 20 phr formulations appear to be holding up better than the 25 phr adhesive. Aging data after 750, 1000, and 1200 hours, as seen in Tables IX, X, and XI, indicates that formulation B, 10 phr antioxidant, is superior to the other two. Formulations A and C appear to be essentially equal over these aging periods. The increase in the spread of joint strengths makes the comparison of formulations less than reliable.

The accumulated data indicates that room temperature strength and strength after short aging periods at 600°F are enhanced by the addition of aluminum powder to the resin. An antioxidant initially reduces R. T. strength; however, upon aging this additive is a must. The better performance of the lower antioxidant concentration indicates some deleterious effect of greater proportions of arsenic thioarsenate.

(3) Stainless Steel Aging at 700°F

Aging the polyimide resin adhesive formulations at 700°F greatly accelerates the thermal decomposition of the resin. The 1/2 hour at temperature data, Table XII, again reflects the drastic reduction of strength shown at 600°F. Joint strength values range from 565 to 840 psi. The two formulations with antioxidant are the lowest in strength. Strengths displayed by the other three range from 630 to 840 psi, with the 25, 1 composition showing the greatest strength.

Twenty-four hours at 700°F clearly shows the benefit of the antioxidant in the formulations. Table XIII gives the average for the neat resin and resin-aluminum formulations as 598 and 366 psi, respectively. Formulation A (20, 1) results in the highest strength at 1917 psi. Adhesives B and C (10 and 25 phr antioxidant) are within 44 psi at 1799 and 1755 psi, respectively.

TABLE VII

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 200 HRS @ 600°F

Adherend: 17-7 PH Stainless Steel, Annealed						
Surface Treatment: Standard Phosphate Etch						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in.)	% R.T. Str.
D	263	537			.003	
	126	257			.002	
	438	913			.003	
Av.		569	656	269		20
E	235	490			.008	
	209	426			.010	
	211	430			.011	
Av.		449	64	29		14
B	1071	2142			.009	
	1048	2096			.009	
	1050	2210			.008	
Av.		2149	114	47		72
A	1093	2231			.008	
	1060	2163			.010	
	998	2100			.011	
Av.		2165	131	53		75
C	1024	2090			.009	
	1039	2211			.009	
	941	1920			.009	
Av.		2074	291	119		71

TABLE VIII

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 500 HRS @ 600°F

Adherend: 17-7 PH Stainless Steel, Annealed						
Surface Treatment: Standard Phosphate Etch						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GIT (in)	% R.T. Str.
D	66	135			.003	
	62	127			.004	
	52	<u>108</u>			.004	
Av.		123	27	11		4
E	Fell Apart During Aging					
B	1091	2182			.008	
	1156	2359			.007	
	1123	<u>2292</u>			.009	
Av.		2278	117	73		76
A	1131	2308			.010	
	1040	2144			.010	
	1042	<u>2170</u>			.010	
Av.		2207	164	72		77
C	1024	2090			.010	
	1102	2119			.010	
	1082	<u>2081</u>			.010	
Av.		2097	38	16		72

TABLE IX

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 750 HRS @ 600°F

Adherend: 17-7 PH Stainless Steel, Annealed						
Surface Treatment: Standard Phosphate Etch						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	Fell Apart During Aging					
E	Fell Apart During Aging					
B	1125	2319			.009	
	1116	2278			.008	
	1269	2538			.007	
Av.		2378	260	114		79
A	826	1686			.012	
	1069	2182			.010	
	1021	2084			.010	
Av.		1984	496	214		69
C	1008	2100			.009	
	976	1992			.010	
	936	1950			.010	
Av.		2014	150	63		69

TABLE X

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 1000 HRS @ 600°F

Adherend: 17-7 PH Stainless Steel, Annealed						
Surface Treatment: Standard Phosphate Etch						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	Fell Apart During Aging					
E	Fell Apart During Aging					
B	972	2025			.009	
	1168	2384			.008	
	1145	2290			.010	
Av.		2233	359	152		75
A	906	1812			.015	
	912	1824			.011	
	1113	2226			.010	
Av.		1956	414	191		68
C	991	2022			.010	
	1077	2244			.010	
	1116	2325			.010	
Av.		2197	303	128		75

TABLE XI

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 1200 HRS @ 600°F

Adherend: 17-7 PH Stainless Steel, Annealed						
Surface Treatment: Standard Phosphate Etch						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	R.T. Str.
D	Fell Apart After Aging					
E	Fell Apart After Aging					
B	1149	2416			.009	
	1121	2242			.008	
	1158	2363			.009	
Av.		2342	174	73		78
A	982	1964			.010	
	1003	2006			.010	
	1053	2171			.009	
Av.		2047	207	89		71
C	934	1868			.010	
	980	2000			.010	
	1057	2033			.010	
Av.		1967	165	71		67

TABLE XII

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 700°F AFTER 1/2 HR @ 700°F

Adherend: 17-7 PH Stainless Steel, Annealed						
Surface Treatment: Standard Phosphate Etch						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	292	596			.006	
	274	554			.003	
	264	<u>544</u>			.005	
Av.		565	42	23		20
E	233	485			.008	
	308	642			.009	
	282	<u>588</u>			.009	
Av.		572	157	65		18
B	288	600			.009	
	308	635			.009	
	516	<u>1075</u>			.008	
Av.		770	475	216		26
A	340	680			.010	
	292	614			.010	
	292	<u>596</u>			.010	
Av.		630	84	36		22
C	409	852			.011	
	408	850			.011	
	384	<u>817</u>			.010	
Av.		840	35	16		29

TABLE XIII

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 700°F AFTER 24 HRS @ 700°F

Adherend: 17-7 PH Stainless Steel, Annealed						
Surface Treatment: Standard Phosphate Etch						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	11	22*			.005	
	262	545			.004	
	319	<u>651</u>			.006	
Av.		598	106	*		21
E	154	321			.008	
	236	492			.008	
	140	<u>286</u>			.008	
Av.		366	206	90		11
B	837	1744			.010	
	908	1853			.010	
	882	<u>1800</u>			.010	
Av.		1799	109	45		60
A	842	1718			.010	
	966	1991			.011	
	1000	<u>2041</u>			.009	
Av.		1917	323	142		67
C	844	1758			.010	
	846	1763			.010	
	924	<u>1743</u>			.010	
Av.		1755	20	9		60

* Value not used to calculate average ultimate strength. Standard deviation was not calculated since a value based on two specimens is not considered reliable.

A 50 hours' exposure to 700°F completely degrades formulations D and E, and those without antioxidant did not survive the aging. Adhesives B, A, and C show joint strengths inversely proportional to antioxidant content. Table XIV lists B (10, 1) at 1575, A (20, 1) at 1558, and C (25, 1) at 1359 psi.

An additional 25 hours' aging results in the loss of the A (20, 1) specimens, as shown in Table XV. Adhesive B (10, 1) results in joint strengths averaging 1243 psi, while adhesive C (25, 1) averaged 848 psi.

After aging 100 hours, formulation B specimens averaged 1109 psi and formulation C 666 psi. Table XVI also gives one value for formulation A at 674 psi. Although such behavior is not uncommon in adhesive joints, the fact that one of the two specimens failing in the aging oven came from the same panel as the one with 676 psi strength is unusual. No explanation is presently available. As shown in the 600°F aging data, the 10 phr antioxidant formulation again produced the most durable joints.

(4) Titanium Tests at Room Temperature

The five adhesive formulations were used to bond cold phosphate etched 8-1-1 titanium. Results of room temperature lap shear test specimens are given in Table XVII. Formulation C (25:1) yielded the highest results, averaging 2087 psi. Formulation B and A gave 1797 and 1677 psi, respectively. These aluminum powder, arsenic thioarsenate formulations did not suffer, due to the additives, as they did on the stainless steel. The neat resin, formulation D, attained a joint strength of 1537 psi, although the aluminum powder filled resin reached only 1339 psi. The difference in bonding the two metals is, then, immediately obvious. Formulation E was highest on steel and the lowest on titanium. These results were obtained with the same cure cycle and essentially the same surface preparation with both adherends. The magnitude of the difference in joint strengths also emphasizes the difference between the two metals, the titanium values being approximately 50% of the stainless steel values. The difficulties in bonding titanium are, therefore, readily apparent.

TABLE XIV

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 700°F AFTER 50 HRS @ 700°F

Adherend: 17-7 PH Stainless Steel, Annealed						
Surface Treatment: Standard Phosphate Etch						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	Fell Apart During Aging					
E	Fell Apart During Aging					
B	754	1508			.008	
	744	1583			.008	
	785	<u>1635</u>			.008	
Av.		<u>1575</u>	127	52		53
A	761	1619			.008	
	731	1492			.008	
	734	<u>1562</u>			.009	
Av.		<u>1558</u>	127	52		54
C	680	1333			.009	
	614	1335			.009	
	677	<u>1410</u>			.008	
Av.		<u>1359</u>	77	36		46

TABLE XV

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 700°F AFTER 75 HPS @ 700°F

Adherend: 17-7 PH Stainless Steel, Annealed						
Surface Treatment: Standard Phosphate Etch						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	Fell Apart During Aging			131	.008	42
E	Fell Apart During Aging					
B	527	1080	320			
	612	1250				
	687	1400				
Av.		1243				
A	Fell Apart During Aging			263	.009	29
C	270	551	639			
	394	804				
	618	1190				
Av.		848				

TABLE XVI

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 700°F AFTER 100 HRS @ 700°F

Adherend: 17-7 PH Stainless Steel, Annealed						
Surface Treatment: Standard Phosphate Etch						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	Fell Apart During Aging					
E	Fell Apart During Aging					
B	543	1131			.009	
	498	1038			.009	
	576	1157			.009	
Av.		1109	119	51		37
A	Fell Apart During Test					
	331	676*			.008	24
	Fell Apart During Test					
C	358	730			.008	
	228	475			.008	
	381	794			.010	
Av.		666	319	138		23

*Represents single specimen at this data point

TABLE XVII

TENSILE SHEAR STRENGTH OF AF-A-2009 FORMULATIONS
AT ROOM TEMPERATURE

Adherend: Ti-8Al-1Mo-1V, Duplex Annealed						
Surface Treatment: R.T. Phosphate Etch (2 min)						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	790	1600			.003	
	760	1520			.004	
	730	1490			.003	
Av.		1537	110	46		100
E	660	1375			.008	
	653	1333			.009	
	642	1310			.009	
Av.		1339	65	27		100
B	950	1920			.009	
	790	1610			.011	
	920	1860			.009	
Av.		1797	310	134		100
A	810	1640			.012	
	820	1650			.014	
	880	1740			.010	
Av.		1677	100	45		100
C	950	1940			.012	
	1120	2220			.015	
	1020	2100			.016	
Av.		2087	280	115		100

(5) Titanium at 600°F

Aging test specimens for one-half hour at 600°F again resulted in a drastic drop from the room temperature values. Losses encountered ranged from 18 to 50%. Results are given in Table XVIII. The greatest loss was by the neat resin. The lowest loss was by the aluminum powder filled resin. Antioxidant addition is not the controlling factor, because loss of strength is not dependent upon the degree of loading.

Comparing the short time at temperature drop with that on the steel adherends shows that except for the neat resin, the drop with titanium is much less severe on a percentage basis. Formulation E (0:1), for example, retains 82% of the room temperature strength on titanium but only 54% on stainless steel.

After 50 hours' aging, joint strengths, as seen in Table XIX, have not only returned to the room temperature strength level but have, in several cases, exceeded them. Formulations A, D, and E actually show an increase in strength while B and C are 8 to 17% below. Formulations A (20, 1) and C (25, 1) are essentially equal at 1743 and 1737 psi, respectively. Formulations C and D are also very close at 1645 and 1678 psi. The importance in this closeness is the fact that formulation D is the neat resin. In all previous tests the neat resin was out-performed by all other formulations.

The 100 hours' data given in Table XX shows that formulation D, the neat resin, gave the high joint strength at 1810 psi. Formulation C gave 1803 psi, while formulation E gave but 1477 psi. Also, note that formulation A, D, and E gave results higher than the room temperature results. The efficiency of the antioxidant in the adhesives on titanium appears to be nil.

Beginning with the 200 hours' data there is a trend showing a greater benefit of the antioxidant. Table XXI lists the joint strengths of antioxidant containing adhesives at over 1700 psi, but the neat resin is 100 psi lower. After 500 hours at 600°F (Table XXII), Formulations A, B, and C gave over 1800 psi joint strength. The neat resin achieved a strength of 1646 psi. The 750 hours' data, Table XXIII, lists adhesives A, B, and C at 1609, 1704, and 1718 psi, respectively. The neat resin reached only 1327 psi. It should be

TABLE XVIII

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 1/2 HR @ 600°F

Adherend: Ti-8Al-1Mo-1V, Duplex Annealed						
Surface Treatment: R.T. Phosphate Etch (2 min)						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	338	704			.003	
	370	771			.003	
	407	839			.003	
Av.		771	135	55		50
E	505	1052			.009	
	563	1149			.009	
	522	1088			.009	
Av.		1096	97	40		82
B	405	827			.008	
	571	1165			.008	
	632	1303			.008	
Av.		1098	476	200		61
A	451	920			.008	
	666	1359			.009	
	753	1537			.010	
Av.		1272	617	259		76
C	457	933			.009	
	633	1292			.008	
	710	1449			.010	
Av.		1225	516	216		59

TABLE XIX

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 50 HRS @ 600°F

Adherend: Ti-8Al-1Mo-1V, Duplex Annealed						
Surface Treatment: R.T. Phosphate Etch (2 min)						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	926	1850	320	132	.004	109
	756	1530			.005	
	823	<u>1650</u>			.004	
Av.		<u>1678</u>				
E	716	1461	167	71	.009	107
	643	1339			.008	
	723	<u>1506</u>			.009	
Av.		<u>1435</u>				
B	790	1600	90	*	.007	92
	828	1690			.008	
	Fell Apart During Test					
Av.		<u>1645</u>				
A	861	1760	50	24	.012	124
	853	1710			.008	
	870	<u>1760</u>			.010	
Av.		<u>1743</u>				
C	861	1630	180	77	.010	83
	868	1770			.010	
	887	<u>1810</u>			.009	
Av.		<u>1737</u>				

*Standard deviation not determined.

TABLE XX

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 100 HRS @ 600°F

Adherend: Ti-8Al-1Mo-1V, Duplex Annealed						
Surface Treatment: R.T. Phosphate Etch (2 min)						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	993	1947			.003	
	878	1722			.004	
	880	<u>1760</u>			.004	
Av.		1810	225	98		118
E	726	1481			.009	
	730	1490			.013	
	718	<u>1465</u>			.010	
Av.		1477	25	10		110
B	920	1840			.009	
	880	1778			.009	
	710	<u>1420</u>			.010	
Av.		1679	420	185		94
A	862	1741			.006	
	815	1680			.011	
	868	<u>1771</u>			.010	
Av.		1731	91	38		103
C	940	1918			.010	
	822	1694			.009	
	898	<u>1796</u>			.009	
Av.		1803	224	92		85

TABLE XXI

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 200 HRS @ 600°F

Adherend: Ti-8Al-1Mo-1V, Duplex Annealed						
Surface Treatment: R.T. Phosphate Etch (2 min)						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	800	1538			.004	
	692	1371			.004	
	999	1998			.005	
Av.		1636	627	265		106
E	769	1569			.010	
	758	1547			.008	
	570	1163			.009	
Av.		1426	406	186		107
B	942	1902			.008	
	681	1352			.008	
	963	1926			.007	
Av.		1730	564	261		96
A	905	1792			.009	
	730	1490			.010	
	955	1910			.009	
Av.		1731	420	177		103
C	757	1514			.009	
	907	1814			.011	
	946	1892			.010	
Av.		1740	378	163		83

TABLE XXII

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 500 HRS @ 600°F

Adherend: Ti-8Al-1Mo-1V, Duplex Annealed						
Surface Treatment: R.T. Phosphate Etch (2 min)						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	868	1702			.004	
	756	1527			.004	
	854	1708			.004	
Av.		1646	181	84		107
E	575	1173			.011	
	740	1510			.009	
	588	1200			.007	
Av.		1294	337	153		97
B	849	1733			.009	
	932	1869			.008	
	1000	2000			.008	
Av.		1867	267	109		104
A	930	1824			.008	
	964	1928			.011	
	865	1765			.011	
Av.		1839	163	67		109
C	905	1810			.010	
	891	1837			.010	
	900	1818			.009	
Av.		1822	27	11		87

TABLE XXIII

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 750 HRS @ 600°F

Adherend: Ti-8Al-1Mo-1V, Duplex Annealed						
Surface Treatment: R.T. Phosphate Etch (2 min)						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	598	1196			.003	
	722	1459			.004	
	663	<u>1326</u>			.004	
Av.		1327	263	107		86
E	628	1256			.008	
	626	1252			.008	
	586	<u>1184</u>			.009	
Av.		1231	72	33		92
B	809	1651			.009	
	722	1459			.009	
	981	<u>2007</u>			.009	
Av.		1704	548	225		95
A	764	1543			.012	
	846	1781			.009	
	737	<u>1504</u>			.013	
Av.		1609	277	122		96
C	847	1694			.011	
	801	1635			.009	
	894	<u>1824</u>			.010	
Av.		1718	189	79		82

noted that after this same period of time the non-antioxidant formulation on stainless steel failed in the aging oven.

The aging of bonded specimens for 1000 hours at 600°F gave the results shown in Table XXIV. Formulations C (25, 1), B (10, 1), and A (20, 1) gave joint strengths of 1909, 1890, and 1743 psi, in that order. The neat resin (0, 0) gave a joint strength of 1750 psi. The averages of the specimens in each formulation retained at least 90% of the room temperature lap shear strength, and in three sets the aged specimens were stronger than the room temperature controls.

At the end of the aging, 1200 hours, the aluminum filled resin shows signs of degradation. The antioxidant-containing formulations continue to provide over 1800 psi joint strength. These data are shown in Table XXV. The neat resin gave an average joint strength of 1469 psi. These results compare very favorably with any other data on these two adherends.

(6) Titanium at 700°F

Results of tensile lap shear data on 8-1-1 titanium adherends with the five formulations, after aging and tests at 700°F are presented in Tables XXVI and XXX. Results after the various aging periods are discussed in the following paragraphs.

The one-half hour data again shows the unexplained drastic drop in strength from the room temperature data. The neat resin formulation D retained only 19% of the room temperature strength at 290 psi. This compares to a 20% retention on stainless steel. The aluminum filled adhesive (E) retained 24% of room temperature strength on titanium at 328 psi but retained only 18% on stainless steel. Formulation B (10 phr antioxidant) at 688 psi represents a retention of 38% on titanium compared to only 26% on stainless. Formulation A (20, 1) shows a 29 to 22% difference in retention on the two adherends. The formulation with 25 phr antioxidant retains 44% on titanium and 29% on stainless steel. This comparison of relative strength retentions serves to point out the basic differences between the bonding of the two metals, i.e., higher initial strength on stainless steel tends to cause greater reduction of strength after short times at elevated temperature, and lesser initial strength appears to lead to a retention of greater fractions of initial strength properties after long-time aging.

TABLE XXIV

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 1000 HRS @ 600°F

Adherend: Ti-8Al-1Mo-1V, Duplex Annealed						
Surface Treatment: R.T. Phosphate Etch (2 min)						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	883	1766			.005	
	931	1862			.004	
	827	<u>1622</u>			.004	
Av.		1750	240	99		114
E	625	1276			.008	
	609	1243			.008	
	594	<u>1188</u>			.005	
Av.		1236	88	36		92
B	941	1882			.011	
	1113	2271			.009	
	751	<u>1517</u>			.009	
Av.		1890	754	308		105
A	724	1492			.012	
	1010	2020			.009	
	841	<u>1716</u>			.011	
Av.		1743	528	216		104
C	836	1672			.010	
	1112	2224			.009	
	906	<u>1830</u>			.009	
Av.		1909	552	232		91

TABLE XXV

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 600°F AFTER 1200 HRS @ 600°F

Adherend: Ti-8Al-1Mo-1V, Duplex Annealed						
Surface Treatment: R.T. Phosphate Etch (2 min)						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	789	1578	278	121	.003	95
	650	1300			.005	
	764	<u>1528</u>			.005	
Av.		1469				
E	444	888	110	48	.008	65
	400	800			.009	
	455	<u>910</u>			.008	
Av.		866				
B	963	1926	363	148	.008	107
	1053	2106			.008	
	863	<u>1743</u>			.008	
Av.		1925				
A	879	1758	182	85	.010	109
	872	1761			.010	
	941	<u>1940</u>			.010	
Av.		1820				
C	964	1928	258	106	.010	97
	890	1816			.009	
	835	<u>1670</u>			.010	
Av.		1804				

TABLE XXVI

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 700°F AFTER 1/2 HR @ 700°F

Adherend: Ti-6Al-1Mo-1V, Duplex Annealed						
Surface Treatment: R.T. Phosphate Etch (2 min)						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	164	335			.004	
	145	296			.004	
	118	240			.004	
Av.		290	95	39		19
E	160	340			.008	
	139	296			.009	
	163	347			.008	
Av.		328	51	23		24
B	536	1094			.004	
	246	502			.009	
	232	469			.009	
Av.		688	625	287		38
A	350	729			.010	
	182	379			.010	
	180	375			.011	
Av.		494	354	166		29
C	392	808			.008	
	386	788			.010	
	554	1154			.010	
Av.		916	356	168		44

Tensile lap shear strength after 24 hours at 700°F, Table XXVII, is shown to retain 50 to 82% of the room temperature value. At this condition Formulation E (0:1) retains 82% at 1102 psi. Formulations A and C show a bond strength of 1331 and 1312 psi, which represents 80 and 63%, respectively, of the room temperature strength. All five adhesive formulations recovered from the 1/2 hour drop.

After 50 hours at 700°F, the antioxidant containing formulations gave higher bond strengths than the other two by a considerable margin. See Table XXVIII. Adhesives B, C, and A yielded strengths of 1131, 1119, and 1089, respectively. Formulations D and E show 847 and 934 psi, in that order.

The 75 hours' data, given in Table XXIX, shows mixed results with formulations A and C below 500 psi, although D and E are 801 and 691, respectively. Formulation B gave a joint strength of 1157 psi. The spread of the individual specimen data at this condition is rather large, as shown in the table.

After 100 hours of aging the antioxidant containing formulations are again better than those without this additive. The neat resin strength of 255 psi should be compared to similar data on stainless steel, where the resin had degraded before 50 hours of exposure. Formulation A yielded the highest strength at this condition at 917 psi. Adhesive B gave 879 psi and Adhesive C 796 psi joint strengths.

The tensile lap shear results indicate that adhesives for use on stainless steel must contain an antioxidant for long-time service at either 600 or 700°F. For titanium bonding an antioxidant is not as necessary at either temperature.

The results show that the strength drop after one-half hour was much more drastic, in general, on stainless steel than on titanium. Also, initial strengths with steel were much higher than with titanium. However, titanium bonded joints retained their strength for much longer periods at elevated temperatures. Based upon the compiled data, formulation B provided the best balance of strength on both metals under all conditions. Formulation A provided the second best balance.

TABLE XXVII

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 700°F AFTER 24 HRS @ 700°F

Adherend: Ti-8Al-1Mo-1V, Duplex Annealed						
Surface Treatment: R.T. Phosphate Etch (2 min)						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	670	1340			.005	
	405	810			---	
	554	<u>1108</u>			.004	
Av.		1086	530	217		71
E	537	1096			.005	
	566	1155			.007	
	527	<u>1054</u>			.009	
Av.		1102	101	41		82
B	407	831			.008	
	420	857			.008	
	491	<u>1002</u>			.008	
Av.		897	171	75		50
A	556	1112			.010	
	760	1520			.009	
	680	<u>1360</u>			.010	
Av.		1331	408	168		80
C	702	1404			.008	
	526	1052			.011	
	740	<u>1480</u>			.009	
Av.		1312	428	186		53

TABLE XXVIII

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 700°F AFTER 50 HR @ 700°F

Adherend: Ti-8Al-1Mo-1V, Duplex Annealed						
Surface Treatment: R.T. Phosphate Etch (2 min)						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	492	965			.005	
	388	761			.004	
	407	814			.004	
Av.		847	204	87		56
E	492	1004			.009	
	431	880			.009	
	441	919			.009	
Av.		934	124	51		70
B	444	888			.010	
	580	1137			.009	
	670	1367			.008	
Av.		1231	479	196		63
A	612	1224			.009	
	360	720			.014	
	662	1324			.010	
Av.		1089	604	264		65
C	664	1328			.008	
	490	980			.009	
	524	1048			.012	
Av.		1119	348	148		54

TABLE XXIX

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 700°F AFTER 75 HRS @ 700°F

Adherend: Ti-8Al-1Mo-1V, Duplex Annealed						
Surface Treatment: R.F. Phosphatate Etch (2 min)						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	631	1260			.006	
	436	872			.005	
	136	272			.004	
Av.		801	988	406		53
E	304	620			.009	
	376	767			.007	
	343	686			.008	
Av.		691	147	60		52
B	550	1122			.008	
	494	990			.008	
	664	1360			.008	
Av.		1157	370	153		65
A	130	278			.011	
	104	212			.005	
	416	849			.010	
Av.		446	637	286		27
C	262	524			.009	
	248	496			.007	
	202	404			.008	
Av.		475	120	51		23

TABLE XXX

TENSILE SHEAR STRENGTHS OF AF-A-2009 FORMULATIONS
AT 700°F AFTER 100 HRS @ 700°F

Adherend: Ti-8Al-1Mo-1V, Duplex Annealed						
Surface Treatment: R.T. Phosphate Etch (2 min)						
Formulation	Maximum Load (lbs)	Ultimate Strength (psi)	Range (psi)	Std. Dev.	GLT (in)	% R.T. Str.
D	140	280			.005	
	110	220			.004	
	130	265			.005	
Av.		255	60	25		17
E	239	478			.009	
	249	508			.010	
	240	480			.008	
Av.		489	30	14		37
B	436	872			.006	
	345	690			.008	
	537	1074			.009	
Av.		879	384	157		49
A	472	963			.010	
	452	904			.009	
	449	880			.008	
Av.		917	83	34		55
C	410	837			.006	
	390	780			.007	
	385	770			.010	
Av.		796	67	30		38

b. Comparison of AF-A-2009 Adhesives To A Commercially Available Polyimide Adhesive

Formulation B, which provided the best balance of tensile lap shear properties with both 17-7 PH stainless steel and Ti-8Al-1Mo-1V titanium alloy adherends, was compared to FM-34 (a polyimide adhesive available from the Bloomington Division of the American Cyanamid Corporation). Figures 10 to 13 show plots of tensile lap shear strength of the two adhesives as a function of isothermal heat aging at 600 and 700°F. All tests were performed at the exposure temperature.

The FM-34 bonded specimens were prepared and submitted by the American Cyanamid Company. The comparison of the two adhesives, therefore, is considered to be valid, since it can be assumed that the supplier of an adhesive has developed a near optimum bonding process for an adhesive before making it commercially available.

The adherends used to prepare the FM-34 bonded specimens received surface treatments different from those for the AF-A-2009 specimens. As described earlier in this report the 17-7 PH stainless steel adherends received the hot phosphate etch pretreatment, while the Ti-8Al-1V-1Mo adherends received the cold (room temperature) phosphate etch. The 17-7 PH adherends bonded with FM-34 received the following pretreatment:

- (a) Steel wool abrasion.
- (b) Acetone wipe.
- (c) Water rinse.
- (d) Immersion for 15 minutes in aqueous solution of Prebond 700 at 200°F. (Prebond 700 is an American Cyanamid Company proprietary material).
- (e) Immersion for 20 minutes in 4% H_2SO_4 and 4% HCL.
- (f) Immersion for 15 minutes in 12% HNO_3 and 2% HF.
- (g) Water rinse.
- (h) Air drying at 150°F.

ADHERENDS: FM-34, Ti-6Al-4V
AF-A-2009, Ti-8Al-1Mo-1V

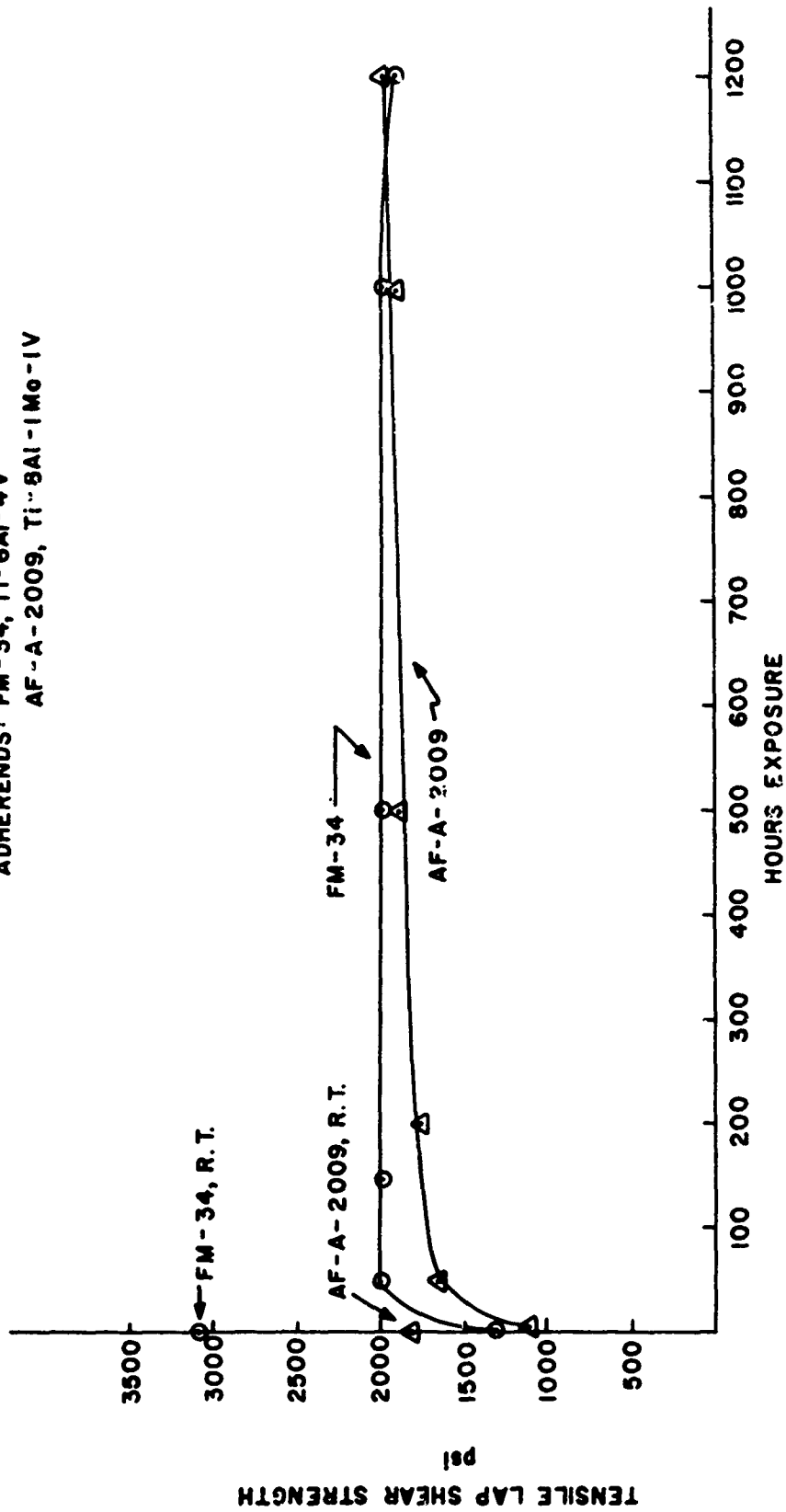


Figure 10. Effect of 600°F Heat Aging on Tensile Lap-Shear Strength of AF-A-2009 and FM-34 Adhesive-Bonded Titanium Joints

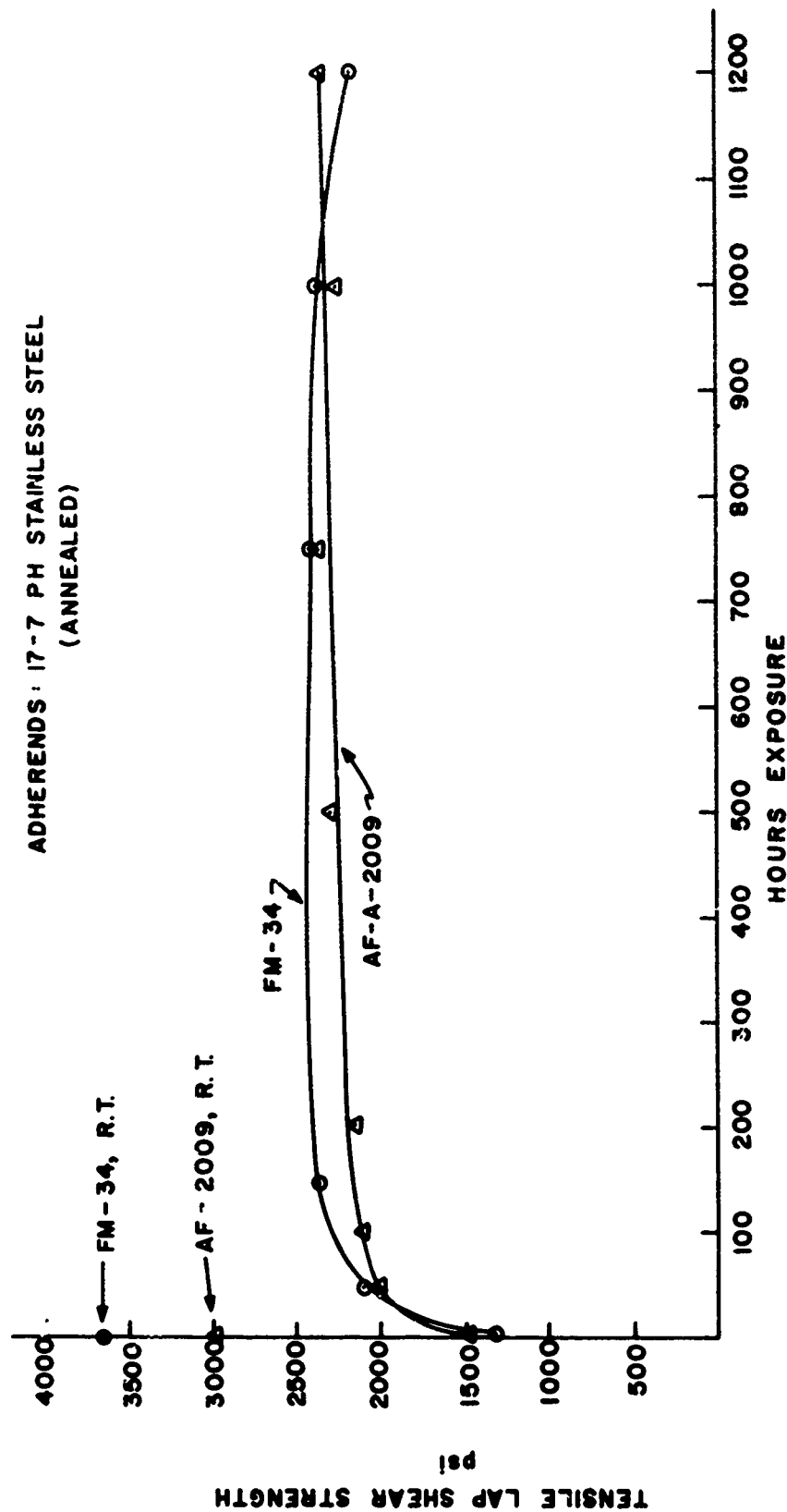


Figure 11. Effect of 600°F Heat Aging on Tensile Lap-Shear Strength of AF-A-2009 and FM-34 Adhesive-Bonded Stainless Steel Joints

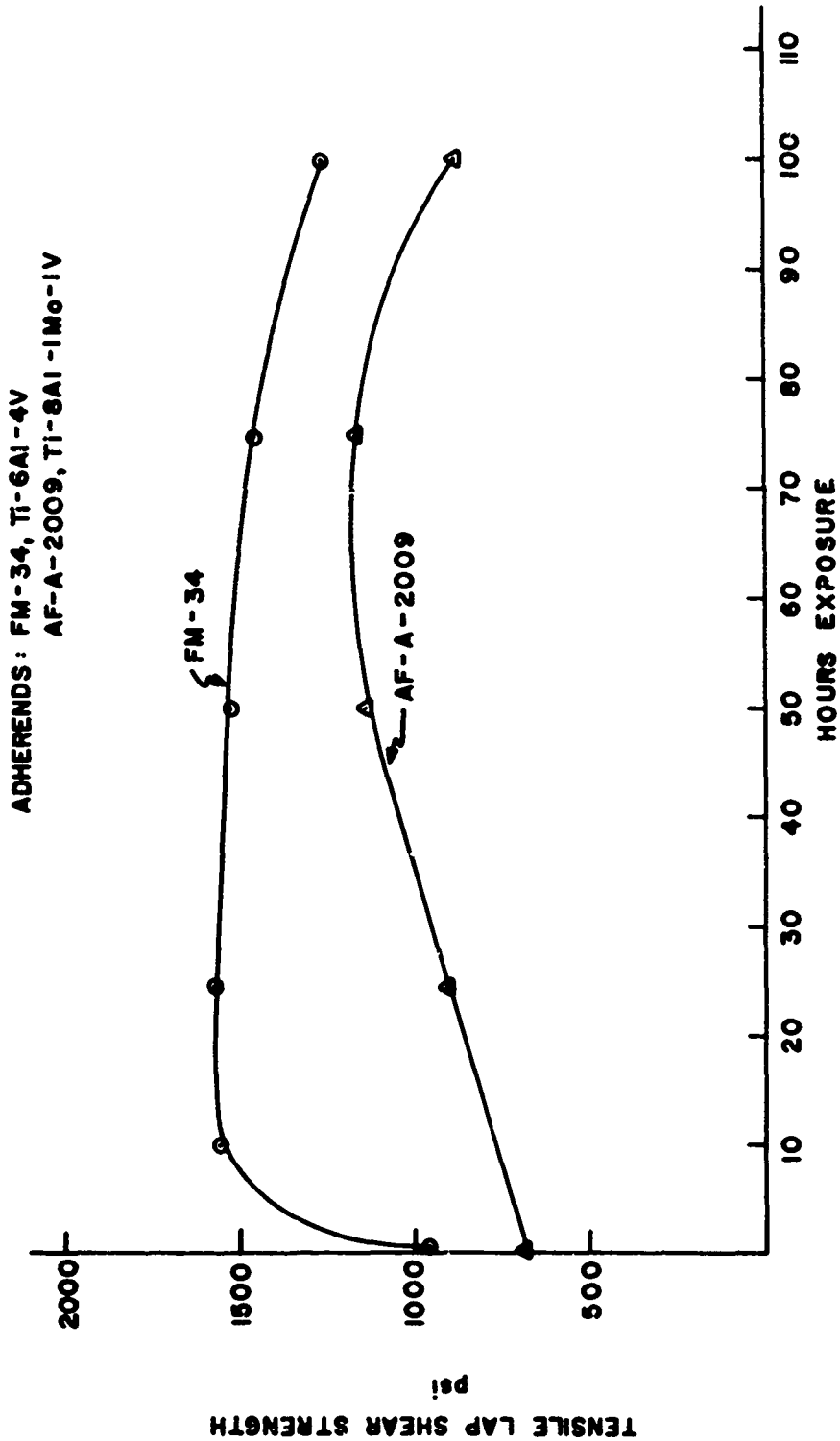


Figure 12. Effect of 700°F Heat Aging on Tensile Lap-Shear Strength of AF-A-2009 and FM-34 Adhesive-Bonded Titanium Joints

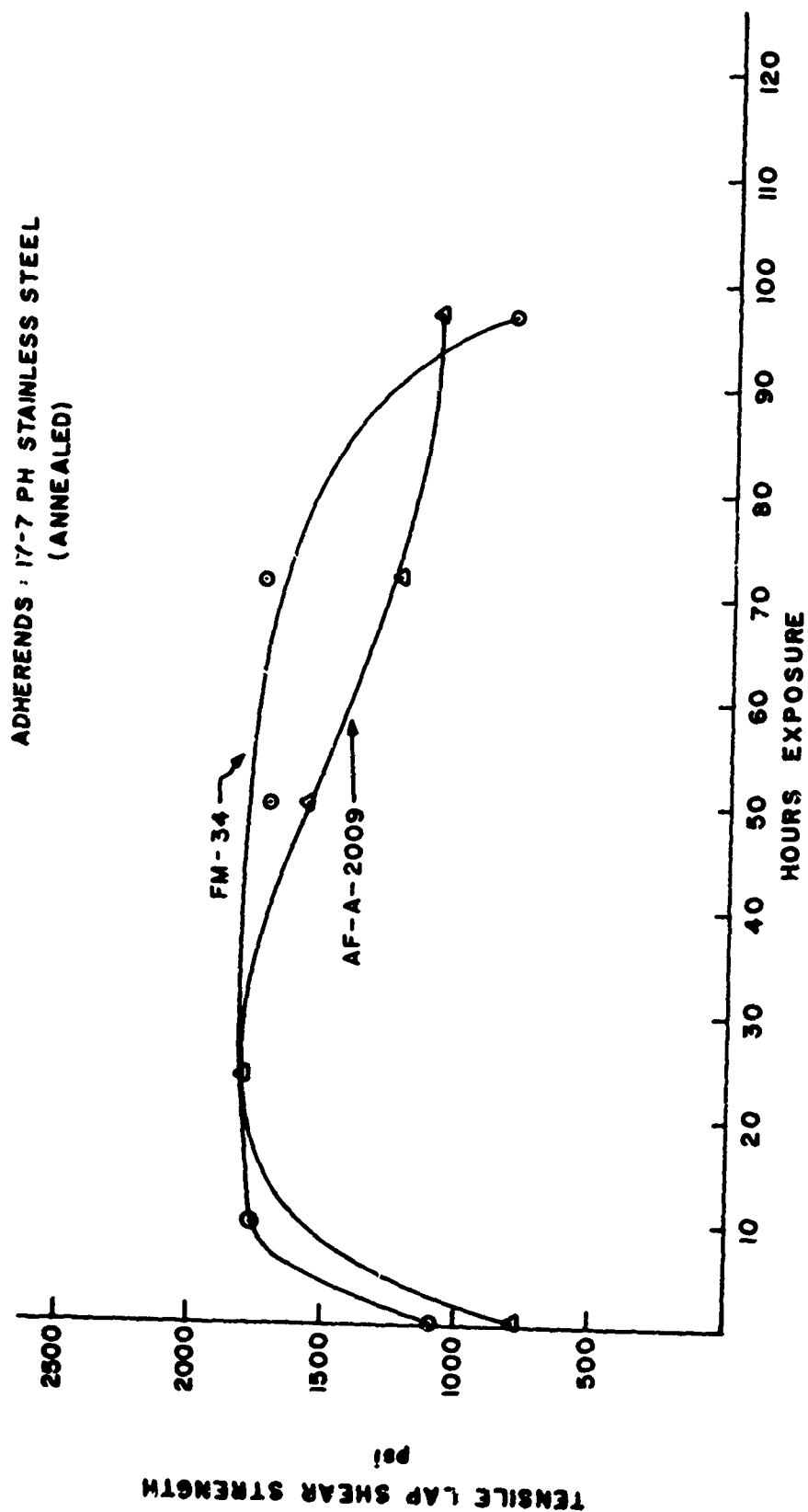


Figure 13. Effect of 700°F Heat Aging on Tensile Lap-Shear Strength of AF-A-2009 and FM-34 Adhesive-Bonded Stainless Steel Joints

The surface treatment used to prepare titanium alloy for bonding with FM-34 was the following (phosphate-fluoride etch):

- (a) Methyl-ethyl ketone wipe
- (b) Sprex cleaning for 15 minutes at 180°F
- (c) Pickling in the following water solution at room temperature for 30 seconds
 - Nitric acid 15% by weight
 - Hydrochloric acid 3% by weight
- (d) Rinse in tap water at room temperature.
- (e) Immersion in the following water solution at room temperature for two minutes:
 - Trisodium phosphate, 50g/liter of solution
 - Potassium fluoride, 20g/liter of solution
 - Hydrofluoric acid, 26ml/liter of solution
- (f) Rinse in tap water at room temperature.
- (g) Soak in 150°F tap water for 15 minutes.
- (h) Spray with distilled water and air drying.

The titanium alloy used as adherends for FM-34 bonded specimens was Ti-6Al-4V.

Figure 10 presents a comparison of the effect of heat aging at 600°F on the tensile lap shear strength of AF-A-2009 and FM-34 titanium alloy bonded joints. The two curves represent strength values which are very nearly identical except that in the time interval from 1/2 hour to 300 hours' exposure, where the AF-A-2009 exhibited 200 to 350 psi lower strength. However, the significant feature of the AF-A-2009 curve was the continual increase in strength as the exposure time was extended. No definite indication of the inception of oxidative degradation, i.e., a loss of tensile-shear properties, was apparent after 1200 hours' exposure. The FM-34 specimens, after the large decrease at 1/2 hour at 600°F to 1280 psi, maintained an essentially constant strength of 2000 psi from 50 to 1000 hours' exposure. The next test

point, 1200 hours, indicated a decrease in strength, possibly caused by the inception of oxidative degradation.

A comparison of room temperature values showed an unexpectedly low strength level for the AF-A-2009 system. Subsequent examination of Ti-8Al-1V-1Mo specimens, which had been subjected to the same pretreatment as the bonded specimens, revealed the existence of a very thin but tenacious iridescent coating on the adherend surface. This coating was presumed to be a scale, formed during the heat treat process, which was not removed during the cold phosphate etch. The presence of scale on the titanium could account for the low room temperature strength.

Figure 11 presents a comparison of tensile shear strength versus heat aging at 600°F of AF-A-2009 and FM-34 bonded 17-7 PH stainless steel joints. The two curves show a small difference of strength levels, 200 psi maximum, during the early stages of heat aging. However, as evident with titanium specimens, the AF-A-2009 bonded specimens continued to increase in strength as heat aging progressed, with no noticeable drop after 1200 hours. The tensile shear strength after 1200 hours' exposure was 2342 psi, 78% of room temperature. The FM-34 specimens showed the beginning of strength degradation at approximately 1000 hours. After 1200 hours' heat aging, the strength was 2180 psi, 59% of room temperature. The superior performance of the AF-A-2009 adhesive, particularly with stainless steel adherends, has been attributed to its improved oxidative stability, compared to that of commercially available polyimides.

The 700°F performance of AF-A-2009 was poorer with titanium adherends, and erratic with stainless steel. Figure 12 shows a comparison of tensile lap shear strength versus time of exposure to 700°F. The FM-34 specimens exhibited a sharp drop in strength after 1/2 hour at 700°F, from 3090 psi at room temperature to 975 psi. However, a rapid recovery of strength was observed after 10 hours, followed by a gradual decrease in strength up to 100 hours. The AF-A-2009 specimens exhibited the sharp drop in strength after 1/2 hour exposure to 700°F but did not have the rapid recovery after continued aging, which is typical of polyimide resins and adhesives. The strength level peaked at approximately 75 hours and fell off significantly by the 100 hours' exposure point.

The comparison of strength retention at 700°F of 17-7 PH stainless steel specimens is shown in Figure 13. The characteristic drop in strength after a short time at elevated temperature was apparent for both adhesives. This initial loss of properties was followed by a recovery with both adhesive systems, peaking at 1800 psi after 24 hours at 700°F. Additional heat aging produced diverging plots up to 75 hours' exposure. The AF-A-2009 bonded specimens exhibited a more rapid decrease in tensile lap shear strength than the FM-34 specimens. Between 75 and 100 hours' exposure, the rate of strength degradation of the AF-A-2009 specimens was reduced, but that of the FM-34 specimens was accelerated precipitously. Extrapolation of the FM-34 curve would result in complete loss of bond strength after a few additional hours of heat aging. Despite the earlier inception of strength loss with the AF-A-2009 specimens, the strength level of specimens bonded with this adhesive were considerably higher than that of the FM-34 system. This fact correlates with the results obtained at 600°F heat-aging conditions.

The peculiar behavior of the AF-A-2009 adhesive in titanium specimens is not clearly understood. It is postulated that the low room temperature strengths achieved with titanium were caused by the presence of the thin layer of scale described earlier. The scale could conceivably also have acted as a cure retardant, since the adhesive appeared to continue to cure as the heat aging progressed, as evidenced by the continual increase in strength. The results of the 700°F exposure with titanium adherends could be indicative of a simultaneous cure and polymer degradation reactions. Exposure to 700°F would cause degradation to proceed at a higher rate with an uncured adhesive than the normal rate typical of a cured adhesive. The large difference in room temperature strength values between the AF-A-2009 specimens and the FM-34 specimens (bonded by American Cyanamid Company) emphasizes the need to develop surface treatments for titanium alloys which will provide reproducible high strength adhesive-bonded joints. In addition, optimization of formulation and cure processes is expected to provide further improvements in initial strength and retention of strength properties after heat aging at elevated temperatures.

c. Infrared (IR) Spectra Study Results

Study by IR analysis was performed as a possible valuable supporting study for the formulation of new adhesives. The indications gained by the instrumental analysis of the formulations when coupled with the resulting bond strengths could provide much pertinent information.

Small portions of the adhesive formulations were analyzed by infrared spectroscopy using KBr pellets. Each formulation was run in the uncured state, after 45 minutes at 212°F and after one hour at 600°F using the same KBr pellet. The procedure was simplified by forming the KBr pellet in a window cut in a strip of 5 mil aluminum foil. A weighed amount of the formulated adhesive/KBr was placed into the window cutout and pressed between steel anvils at about 18,000 psi. The aluminum foil served to control the pellet thickness and provide a means of identification as well as a relatively rigid sample holder. A similar pure KBr pellet was prepared to serve as a reference in a double beam spectrophotometer.

Each prepared sample was run in the uncured state to serve as the reference for polymer changes due to heating. Each sample was then heat aged (staged) at 212°F for 45 minutes and given a second spectra run on the same graph as the uncured sample. This procedure was repeated after aging each sample one hour at 600°F. The spectra, therefore, follow the progress of curing exactly as the adhesive in the bonded joint. It is recognized that there may be some alteration of the adhesive due to the presence of the prepared adherend.

The complexity of the spectra precludes a complete interpretation of each of the 15 spectra. However, it was considered reasonable to obtain a fair interpretation of the neat resin, formulation D. Major bands and identifiable peaks were selected and are listed in Table XXXI. Consideration of the intensity of adsorption of each peak in successive runs verifies the disappearance or appearance of certain structural moieties present in the resin. These can be assigned to one or more of the resin constituents.

TABLE XXXI

Infrared Adsorption Peaks

Formulation D, AF-R-2009 in KBr								
Band	Run #1		Run #2		Run #3		WN	Assignment
	Peak	Disc.*	Peak	Disc.	Peak	Disc.		
2.7- 3.1	2.75	SB	2.75	SB	2.75	Ws	3636	O-H Glycol
	2.85	SB	2.85	SB	2.85	Ws	3508	O-H Glycol
	2.92	SB	2.92	Ss	--	--	3425	N-H Amine
	3.04	SB	3.04	Sp	--	--	3289	N-H Amine
3.1- 3.3	--	--	--	--	3.18	Ws	3145	C-H ?
	--	--	--	--	3.24	Wp	3086	C-H ?
3.3- 3.6	3.40	SS	3.40	SS	--	--	2941	C-H ₂ Glycol
	3.47	SS	3.47	Sb	--	--	2882	C-H ₂ Glycol
3.7- 3.9	3.77	Mb	3.79	Mb	--	--	2653	O-H Glycol Acid
	3.84	Mb	3.90	Mb	--	--	2604	O-H Glycol Acid
5.0- 5.2	5.08	Mp	5.08	Mp	--	--	1969	O-H Hydrogen Bonded
	5.17	Mp	5.17	Mp	--	--	1934	O-H Hydrogen Bonded
5.3- 5.4	--	--	--	--	5.38	Ws	1858	C=O Anhydride
5.3- 6.1	5.64	MS	5.64	MS	5.64	SS	1773	C=O Imide
	5.78	SS	5.78	SS	5.78	SS	1730	C=O Imide
	5.83	SS	5.83	SS	5.83	SS	1715	C=O Diester
	5.88	SS	5.88	SS	--	--	1701	C=O Diester
	5.95	SS	5.95	Sb	5.95	Mb	1681	C=O Amide
	6.03	SS	--	--	--	--	1658	C=O Aryl Ketone
	6.24	SN	6.24	SN	6.24	MS	1603	C=O Carboxylate
6.1- 6.6	6.45	Sp	6.45	Sp	--	--	1550	C=O Carboxylate
	6.69	SS	6.69	SS	6.69	SS	1495	C-H Ring
6.6- 7.0	6.88	Sp	6.88	Ss	6.88	MS	1453	CH Ring ?
	--	--	--	--	7.00	MS	1429	C=O Carboxylate
7.1- 7.4	7.24	SB	7.24	SB	7.24	Ss	1379	C=O Carboxylate
	--	--	--	--	7.38	Sb	1355	C=O Carboxylate
7.4- 8.4	7.68	SB	7.68	SB	7.68	Ms	1302	C-N Diamine
	7.73	SB	7.73	SB	7.73	Ms	1294	C-N Diamine
	8.05	SB	8.05	SB	8.05	MB	1242	CN Diamine
	8.37	SB	8.27	SB	8.37	MN	1195	CN Diamine
8.5- 9.2	--	--	--	--	8.57	MS	1167	C-N Amide
	8.78	SB	8.78	SB	--	--	1139	C-O Diester
9.2- 9.9	--	--	--	--	9.06	SB	1104	C-O Anhydride
	9.30	SB	9.30	SB	9.30	MB	1075	C-OH Glycol
9.9-10.4	9.60	SB	9.60	SB	--	--	1042	C-OH Glycol
10.7-11.1	--	--	--	--	10.1	WS	990	C-H Ring
11.1-12.0	--	--	--	--	10.8	WB	926	C-H Ring
12.3-13.0	11.70	SB	11.70	SB	11.70	WB	855	C-H Ring
13.1-14.2	12.65	B	12.65	MB	12.65	WS	792	C-H Ring
	--	--	--	--	13.43	WS	744	C-H Ring
	--	--	--	--	13.95	SB	717	C-H Ring

*S-Strong, M-Medium, W-Weak, B-Broad, b-Less broad, S-Sharp, s-Shoulder, p-pip, N-Narrow

Formulation D will be discussed in some detail in the following section. The experimental adhesives will be discussed, in less detail, in order of increasing formulation. In the latter, only noticeable differences between the neat resin in the "as received" and the "as cured" state will be discussed.

(1) Formulation D

The spectra for formulation D, the neat resin, are shown in Figure 14. As given in Table XXXI, the first strong, broad band is attributed to the O-H groups of the glycol and the N-H groups of the amine. This band decreases in intensity in successive runs, indicating the disappearance of these compounds. The second band, 3.1 to 3.3 μ , appears only in the cured resin as a weak but sharp peak. Some difficulty in assigning this peak was encountered; however, the literature lists vibrations of C-H of an unsaturated ether in this area. The presence of any such material in the resin cannot be accounted for at this time.

The next three bands, 3.3 to 3.6 μ , 3.7 to 3.9 μ , and 5.0 to 5.2 μ , all appear to be related to the glycol present. As indicated, assignment is made to C-H's, O-H's, and hydrogen-bonded O-H groups. The 5.3 to 5.4 μ band appears in the cured resin spectra and the literature ascribes this band to the C = O group of a cyclic anhydride. This band is also perplexing, since it appears that some ester or amide is reverting to the anhydride upon curing. This is more suggestive of a degradation than a curing mechanism. However, the band is there for the reader's contemplation.

The following band, spanning the spectrum from 5.5 to 6.1 μ , with many strong, sharp peaks, is assigned to the carbonyl (C = O) group of various components. The 5.6 μ peak and the 5.78 peak are attributed to the polyimide. The increasing intensity of the former tends to verify the formation of this compound. Peaks at 5.88 and 6.03 μ do not appear in the cured resin; indications are that these are the result of the disappearance of the ester groups during cure. Those at 5.83 and 5.95 μ are assigned to an ester group and an amide group, respectively. The presence of these indicates that the resin is not fully cyclized, i.e., the cure is not complete.

- 1 - Initial Film
- 2 - 45 Minutes at 212OF
- 3 - 45 Minutes at 212OF and 1 Hour at 600OF

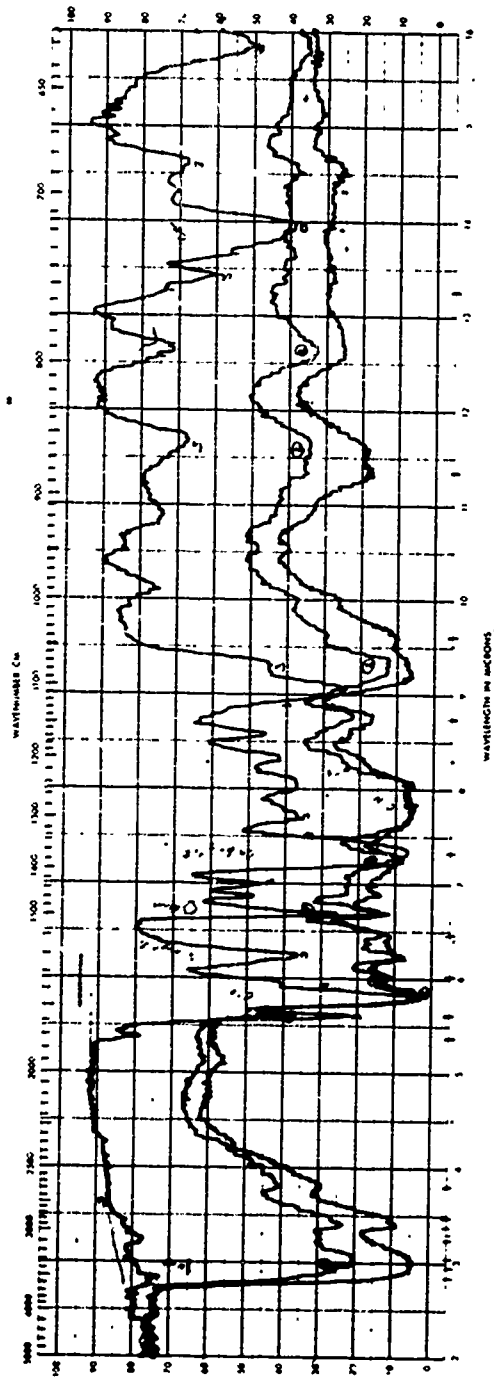


Figure 14. IR Spectra of AF-A-2009, Formulation D, on a KBr Salt Window

Formation of carboxylate ions is indicated by the band from 6.1 to 6.6 μ . Both peaks tend to weaken on curing. In the same category are the peaks in the band 7.1 to 7.4 μ ; however, here the 7.00 and 7.38 μ peaks are predominant in the spectra of the cured resin. A stable carboxylate ion appears in all three runs at 7.24 μ . There appear to be two separate moieties represented in the band from 6.6 to 7.0 μ , probably C-H vibrations of the various ring structures. One remains strong through the curing, while the 6.88 μ peak weakens.

Peaks assigned to the C-N of an amine are represented in the band from 7.4 to 8.4 μ . All four peaks weaken upon curing except that at 8.37 μ . This peak appears in run No. 3, the cured resin. This appears to be closely related to the 8.57 μ peak due to the appearance of an amide functionality. Continuing with the band from 8.5 to 9.2 μ , the 8.78 μ peak, due to a diester linkage, disappears on curing. In spectra No. 3, a peak appears at 9.06 μ , presumably due to the C-O of an acyclic anhydride. This peak tends to verify the 5.38 μ peak mentioned above.

Glycol disappearance is indicated by the weakening of the 9.2 and 9.9 μ band. At 10.1 μ , in the band from 9.9 to 10.4 μ , the weak peak appears to be due to the 1,2,4 trisubstituted benzene ring of the benzophenone. It appears that this peak and the following peak (10.8 μ) become apparent due to the increasing cyclization of the resin. The peaks representing the next band, 11.1 to 12.0 and 12.3 to 13.0 μ , are due to the C-H's of the ring structures. The last two peaks appearing in the spectra of the cured resin are also attributed to C-H of the various rings. The reason for this appearance after curing is not understood.

Almost without exception then the infrared spectra verifies the general occurrence of the reactions during the polymerization of the polyimide resin. It can be expected that similar reactions will occur in the formulated adhesives, with some variations due to the additives.

(2) Formulation E

This formulation contains 100 phr aluminum powder primarily to reduce the thermal expansion of the resin. Although aluminum powder is added to the

resin it is recognized the powder is aluminum oxide. The IR spectra are shown in Figure 15.

A comparison of the uncured formulation spectra with that of the neat resin shows few differences. The chief difference occurs at 5.62μ ; in formulation D there was a definite imide carbonyl bond at that point. In formulation E, the indication was very faint. Formulation D also contains a 7.00μ peak which is not present in E. This indicates the absence of one carboxylate ion providing group. At 10.55μ lies another difference. There is no such peak in the uncured filled resin. However, this peak does occur in run No. 2 but not in No. 3. This peak probably represents C-H out-of-plane bending vibrations. The uncured filled resin also has a peak at 13.8μ , which like many peaks in this region may be C-H out-of-plane bending associated with ring or, as in this case, perhaps an amide bond (Amide V 720 cm^{-1}).

Thus, none of the differences can be attributed to the aluminum powder. Any influence of the powder on the uncured resin must be, therefore, very subtle indeed. Perhaps the examination of the cured resins may be more revealing.

There are a number of differences between the spectra of the uncured resin and the cured resin, i.e., differences not expected from a study of the neat resin. The following peaks will be discussed: 1) in cured resin, 5.62 , 5.97 , 6.69 , 10.95 , and 13.2μ ; and 2) in uncured resin, 9.25 , and 9.9μ .

The first three are rather subtle differences which a finer spectrum could eliminate. The 5.62μ peak of the imide carbonyl was discussed previously. The 5.97μ peak, also a carbonyl, is shown clearly in the cured resin but it tends to be lost in the 6.03μ peak in the uncured resin. The same can be said for the 6.69μ peak, the broad band in the uncured resin does not appear to cover this peak. The 10.95μ peak is quite evident in the spectra and indications are that this represents the O-H bending of a dimer or even perhaps a metal oxide. The 13.2μ shoulder is probably the result of a ring C-H. Occurring in the uncured resin, the peak around 9.25μ is part of a larger adsorption band which all but disappears upon curing. A portion of this could be masked by the emergence of the strong 9.04μ peak. The 9.2μ band is in part a glycol OH band

- 1 - Initial Film
- 2 - 45 Minutes at 212°F
- 3 - 45 Minutes at 212°F and 1 Hour at 600°F

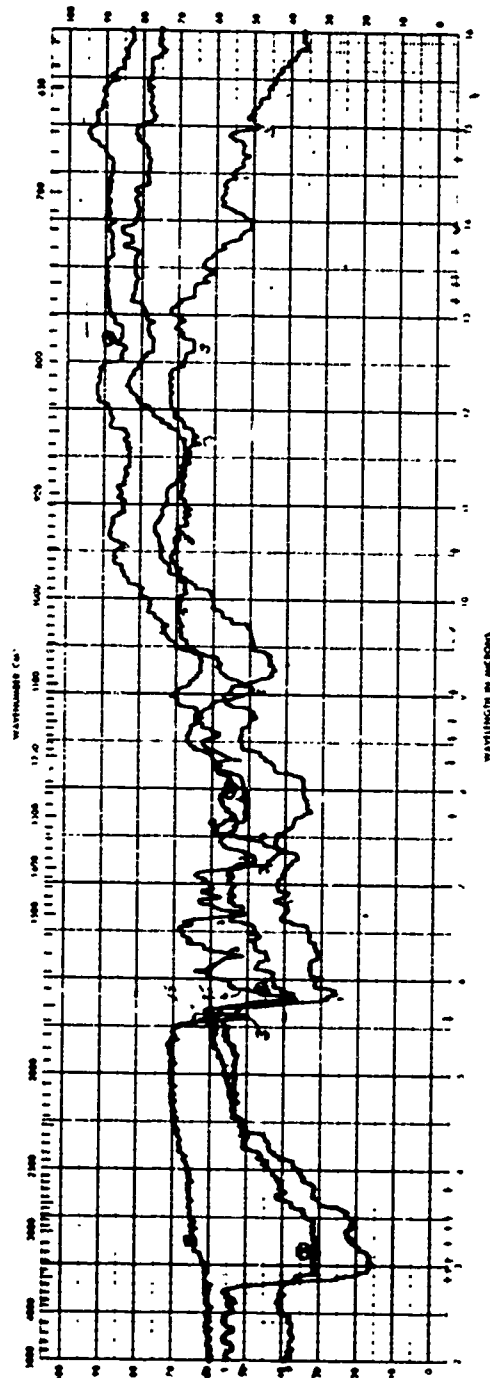


Figure 15. IR Spectra of AF-A-2009, Formulation E, on a KBr Salt Window

while the 9.04μ appears to be due to an anhydride band. The 9.9μ is also due to a glycol type of linkage which disappears upon curing the resin.

A comparison of the spectra of the two formulations, as cured, reveals only a few differences in E that are not in D. These include 6.58 and 14.45μ peaks, both of which are weak. The former may be due either to the skeletal stretching of the rings, possibly an amide bond, or to N-H deformation. The latter again may be assigned to the C-H bending of the rings.

The spectra of D, as cured, contain more peaks than the formulated resin, including peaks at or near 2.85 , 3.24 , 5.38 , 10.0 , 10.6 , 13.65 , and 14.9μ . Many of these have been assigned in preceding sections as 2.85 glycol, 3.24 C-H, 5.38 anhydride, 10.0 glycol, and 10.6 C-H ring. The two remaining peaks, all weak in intensity, are assigned as follows: 13.65μ possibly amide band probably C-H bending, and 14.9 C-H bending in aromatic rings.

In reviewing this phase of formulation E, several things can be mentioned, e.g.: 1) the cured resin is a better adhesive, 2) the aluminum tends to act as a catalyst to the resin, and 3) aluminum oxide does not appear in the spectra.

(3) Formulation C

Arsenic thioarsenate was added to the combination of resin and aluminum powder of Formulation E on a 20 phr basis. The compound has been found to be a highly efficient antioxidant in other aromatic heterocyclic polymers such as polybenzimidazole (PBI). The spectra of this formulation, Figure 16, could show the presence of the arsenic compound or arsenic-aluminum compounds.

Comparing the uncured formulation spectra to that of the neat resin shows a greater definition of peaks in the latter at 3.16 , 3.23 , 3.65 , 4.33 , and 5.25μ . The spectra of C contains but one peak not seen in D; this is at 14.13μ . And the D spectra contain only one peak of significance, this being at 7.00μ . The 14.13μ is probably a C-H out-of-plane bending of the ring structures present. It is noted that this peak is present in the cured neat resin. Carboxylate ions probably account for the peak at 7.00μ . This peak was missing in formulation E as well. Neither the antioxidant nor the metal powder is apparent in the uncured material.

- 1 - Initial Film
- 2 - 45 Minutes at 212°F
- 3 - 45 Minutes at 212°F and 1 Hour at 600°F

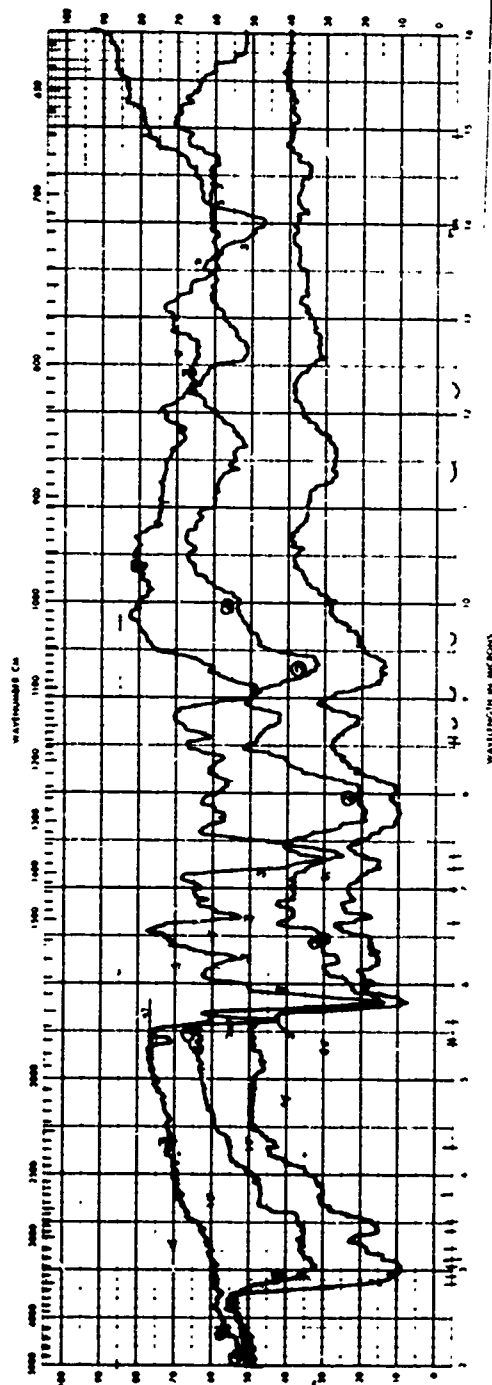


Figure 16. IR Spectra of AF-A-2009, Formulation C, on a KBr Salt Window

The chemistry of this formulation, by comparing uncured versus cured resin spectra, does not appear to be affected by the additives. All uncured resin peaks up to 5.3μ disappear or decrease upon curing. The anhydride peak (5.38μ) appears and the 5.62μ peak intensifies from a shoulder on the carbonyl peak as expected. Most other peaks appear or disappear as expected, except for a small change at 9.12 and 11.83 where the peak appears as a doublet. At the 12.1 to 12.4μ region, where there is a definite adsorption due to the C-H out-of-plane deformation of a 1,2,4-trisubstituted benzene, the 11.83μ peak assignment could not be made due to a limited selection, cyclic ether, peroxide, or an S-C-S group. There appears to be little if any change in the chemistry of the resin due to the additives. The effect seems to be one of masking some areas and unmasking others.

A comparison of the cured formulations D and C shows that there are some indications of changing chemistry. These changes lie primarily in the region from 3 to 5.0μ . However, due to the spectra sensitivity, it is impossible to state the changes with certainty. If these are in fact changes due to the antioxidant, the following formulation, in which the antioxidant concentration is increased, should show more. Other changes appear at 6.43μ , the already discussed 11.83μ and 12.2 - 12.4μ , and at 13.05μ . The 6.43μ peak is due to a carboxylate ion which is persisting through the cure cycle. The 13.05μ change again appears to be due to changing influences on the ring structures (C-H).

(4) Formulation A

Formulation A contains 20 phr of the arsenic thioarsenate antioxidant used in the previous formulation. As with many additives, a composition was sought which provided a synergistic effect between the components. Such an effect could provide the extra measure of thermal/oxidative stability required for the adhesive. The spectra are shown in Figure 17.

A comparison of the spectra of the uncured resins of formulations D and A discloses several differences: the hydroxyl-amine band of A defines several peaks not readily apparent in D at 3.02 , 3.06 , 3.13 , and 3.27μ . They are probably included in the broad band in that region. A significant difference

- 1 - Initial Film
- 2 - 45 Minutes at 212°F
- 3 - 45 Minutes at 212°F and 1 Hour at 600°F

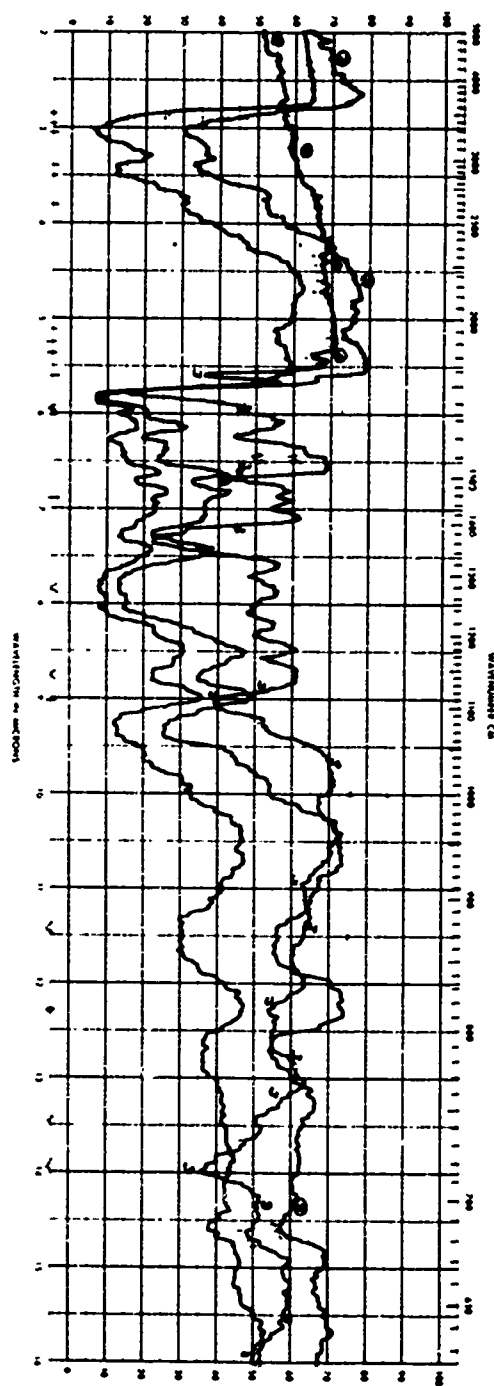


Figure 17. IR Spectra of AF-A-2009, Formulation A, on a KBr Salt Window

occurs in the region of 4.7 to 5.0 μ . The peaks of this band are shown more clearly in the spectra after B-staging treatment (4.83, 4.87, and 4.96 μ) for which literature listed correlations do not appear applicable. There is also a difference between spectra at the 5.62 to 5.64 μ region. In formulation A spectra, both of these are part of the 5.80 μ peak as shoulders. These are the carbonyl imide peaks in both cases. The last difference appears at 9.8 to 9.9 μ in the A formulation spectra; this peak appears to be that of the C-N group of an amine.

Although an increase in the number of peaks was expected due to the inclusion of the additives, this is not the case. Rather, the net effect seems to be a broadening of peaks, some almost to extinction. The 7.00 μ and 13.04 μ peaks of the uncured neat resin do not appear in the adhesive formulation. These are due to the carboxylate and ring C-H's, respectively. Peaks at 13.53 and 14.95 μ in the neat resin spectra which are not seen in the formulations are attributed to ring C-H's.

The spectra of formulation A in the cured and uncured states show only three differences from the expected behavior of the resin itself. These are at 5.95, 6.58, and 12.3 μ . The uncured formulation shows a peak at 6.53 μ , which is also apparent in the B-stage run, as a shoulder on the 6.45 μ peak. The strength of this peak indicates that it is probably an amide II band resulting from C-N and N-H vibrations. The 5.95 μ is undoubtedly a carbonyl stretching; however, since it does not appear in the uncured adhesive it is probably not due to the reactants but to some secondary reaction such as the formation of an aryl carboxylic acid. This reaction is deemed possible early in the cure. The 12.3 μ peak, again occurring in the cured resin, has been seen in the other formulations and assigned to the C-H out-of-plane bending of an aromatic ring, particularly a 1,2,4 trisubstituted benzene.

A comparison of the cured formulation and the cured neat resin spectra shows two differences occurring in the formulation at 6.4 and 12.3 μ . A shift of peak is apparent between the two materials at about 10.8 μ . The 6.4 μ peak indicates the N-H vibration of a secondary amine, and the 12.3 μ peak is as indicated in the paragraph above. In the formulated resin an adsorption band exists from 10.6 to 11.2 μ with the most intense peak at 10.95 μ . The neat

resin shows this band in the same region; however, the peak is centered about 10.85μ , and is broader. The broad peak in this range has been assigned to OH out-of-plane bending of a carboxylic acid. The influence of the many polar moieties present is probably responsible for the shifting in the formulated material¹.

(5) Formulation B

The last formulation B, contains 25 phr of the arsenic thioarsenate antioxidant with the resin/aluminum powder ratio at 1 to 1. This formulation will provide the necessary comparison of the effect of the antioxidant with formulations C (10 phr) and A (20 phr). The spectra are shown in Figure 18.

The spectra of the uncured formulation again follows that of the neat resin rather closely, showing only changes in formulated resin in the 4.6 to 5.0μ region and at 15.05μ , and at 10.55 and 14.95μ in the neat resin. The formulated resin again shows weak peaks at 4.73 , 4.80 , 4.83 , 4.87 , and 4.94μ , for which the literature lists a variety of correlations, none of which appear reasonable at this point. The 15.05μ peak approximates a peak in the neat resin spectra at 15.13μ ; however, the peak width and intensity indicate a difference in the source. C-H out-of-plane bending evidently accounts for both peaks. The neat resin shows a peak at 10.55μ which is attributed to vibrations of a carboxylic acid, dimer, O-H. The 14.95μ peak is assigned to the vibration of ring C-H's.

Differences between the spectra of cured and uncured formulation B are in the region of 4.8 to 5.3μ , at 11.2 to 11.4μ , at 12.16μ , and at 12.85μ . The first is that region in which no assignment has been made. The 11.2 to 11.4μ range is considered to be due to vibrations of a cyclic ether or an amine acid (NH_3^+ rocking). The 12.85μ peak is once again due to ring C-H bending. The above listed bands were present in only the uncured formulated material. One peak was apparent in the cured resin and not seen in the uncured resin. This was at 12.16μ . Although a weak peak, it is noted because it begins a general band seen only in the cured formulation. It appears first in the spectra after B-staging, at around 12.1μ . However, this peak is also probably due to the ring C-H's.

- 1 - Initial Film
- 2 - 45 Minutes at 212°F
- 3 - 45 Minutes at 212°F and 1 Hour at 600°F

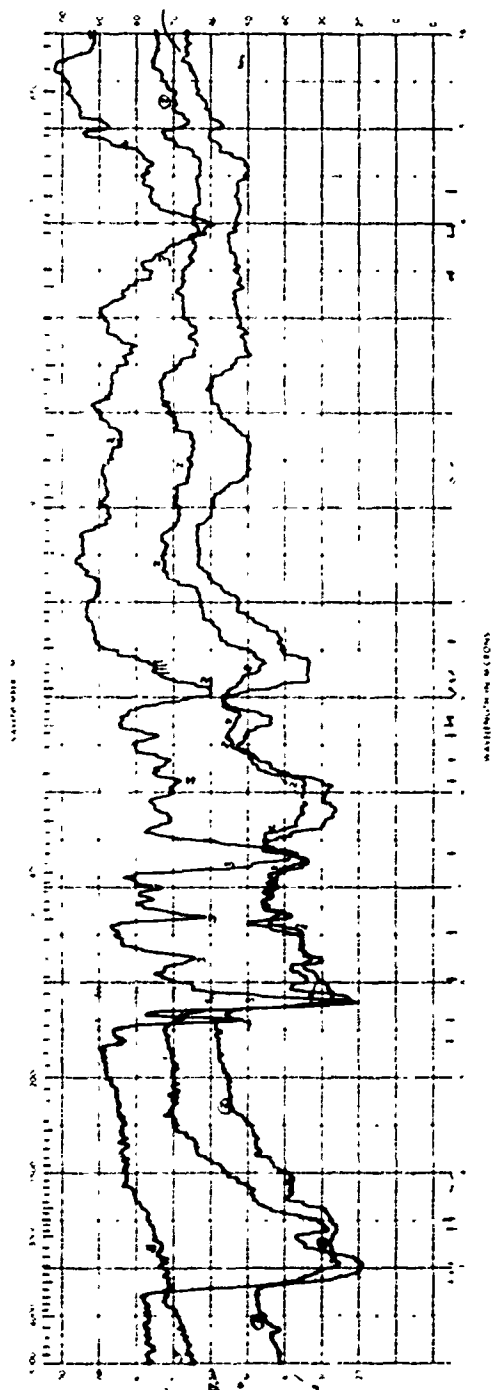


Figure 18. IR Spectra of AF-A-2009, Formulation B, on a KBr Salt Window

(6) Summary

Through this infrared study of the various formulations the following comments can be made:

- 1) Aluminum powder as an additive cannot be seen in any spectra.
- 2) Arsenic thioarsenate additive cannot be seen in any spectra.
- 3) The influence of the additives aluminum and arsenic thioarsenate can be seen in various regions of the spectra.
- 4) The perturbations in the region 6.5μ are attributed to the aluminum powder.
- 5) The region around 4.5 to 5.0μ appears to be due to the arsenic compound.
- 6) The weak absorptions around 12.2 to 12.4μ also appear to be due to the arsenic compound.
- 7) The spectra show that the uncured resin may show some polyimide linkages.
- 8) During the cure some amide/ester groups revert to the anhydride (5.38μ peak).
- 9) The presence of low-molecular-weight species in the cured neat resin (2.75 , 2.85 , 3.18 , and 3.24μ) could contribute to the earlier degradation of the neat resin upon exposure to high temperature.
- 10) The curing of the formulations tends to reduce the number of and intensity of the peaks.
- 11) The presence of peaks attributed to carboxylic acid, carboxylate, anhydride, diester indicates that many of the proposed reactions may take other routes and that the reactions are not complete.
- 12) From this study it has been learned that IR spectra cannot differentiate between high and low strength adhesives, nor can thermal stability be established from IR spectra.

SECTION IV

SUMMARY

Experimental adhesives based on the AF-R-2009 polyimide resin system have been evaluated with Ti-8Al-1V-1Mo and 17-7 PH stainless steel adherends. The adhesives have demonstrated a definite capability for use in high temperature applications for extended periods. Formulation B, containing 100 phr of aluminum powder and 10 phr of arsenic thioarsenate, has exhibited an excellent retention of strength properties during the exposures described in this report. Formulation B has exhibited oxidative stability and strength retention properties equivalent to the commercially available polyimide adhesive, FM-34, with titanium adherends after long-time exposure to 600°F and with 17-7 PH stainless steel after long-time exposure to both 600 and 700°F. Further development effort to optimize the cure and the formulation is recommended.

The infrared studies of the adhesive formulations, although somewhat disappointing, have given sufficient promise in the identification of various functional groups within the system to warrant continuing such procedures. More detailed spectra analysis may yet provide other necessary evidence to enable the discernment of optimum compositions.

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